STORMWATER RUNOFF TREATMENT BY FILTRATION: A PILOT-SCALE STUDY

DISSERTATION RESEARCH PROPOSAL

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CHAPTER 1 - LITERATURE REVIEW: URBAN RUNOFF

Infiltration of stormwater runoff has long been an accepted practice for the disposal of stormwater and replenishment of groundwaters in many locations in the United States. With the advent of urbanization, many of the natural infiltration areas have disappeared permanently, due to both covering the land with roads and buildings and to the regrading and compacting that accompanies construction. Along with the decrease in area available for infiltration, the volume of runoff from urban areas has increased, as has the runoff's pollutant loadings. Some of this urban runoff may not be suitable for replenishing groundwater due to its pollutant loading from the surfaces over which it flows. Investigation of treatment systems for this runoff is an on-going process; however, there is little information available that compares the various treatment devices. Two recent works that compare the performance

of some of the treatment devices are Claytor and Schueler's <u>Design of Stormwater Filtering Systems</u> (1996) and Herrera Environmental Consultants' work for the City of Bellevue, WA (1991 and 1995).

Because of the manner in which storm drainage systems are designed and constructed, the untreated runoff from problem areas is combined at its inflow point to the storm sewer system with runoff already in the system. This combined runoff typically is directly discharged into surface waters, or occasionally to groundwaters. It is unlikely to be treated prior to discharge to either receiving water. Even if the runoff were to be treated at the 'end of the pipe' prior to its discharge, the volume of runoff is so large that treatment facilities would be very expensive to construct and maintain. In some locations, stormwater runoff is combined with sanitary wastewater and the combined flow is directed toward the municipal wastewater treatment plant. However, in most cities with these combined sewers, the volume of water to be treated during and immediately following a rain event is too large to be completely treated. Much of the combined sewage bypasses the treatment plant (combined sewer overflow 'CSO') and may be only partially treated (coarse screening and disinfected) before discharge. Treating runoff from critical source areas before it is combined with runoff from other areas is more cost-effective.

To prevent harm either to the surface waters or to the groundwater, the stormwater runoff from problem source areas or stormwater hotspots needs to be treated. Stormwater hotspots are those places where generation of significantly higher concentrations of hydrocarbons, toxic trace metals, or other toxicants may occur. Examples of these hotspots include the following: airport deicing facilities, auto recyclers/junkyards, commercial nurseries, parking lots, vehicle fueling and maintenance stations, bus or truck (fleet) storage areas, industrial rooftops, marinas, outdoor transfer facilities, public works storage areas, and vehicle and equipment washing/steam cleaning facilities (Bannerman, Owens, Dodds, and Hornewer, 1993; Pitt, Field, Lalor, and Brown, 1995; Claytor and Schueler, 1996). Rather than treating the large volume of runoff at the end of the pipe, one potentially cost-effective approach is to treat the runoff from the specific problem sources before it mixes with the runoff from the majority of 'non-problem' areas, such as residential developments, institutional developments, and non-industrial rooftops (Pitt, et al. 1995; Claytor and Schueler, 1996). Single, small point-source treatment devices have been developed and are currently being marketed. Most of these treatment devices, however, are designed to remove settleable solids, not colloidal or soluble pollutants. Only recently are these in-line treatment devices beginning to use filtration as a planned treatment step to remove the colloidal and soluble pollutants.

Characteristics Of Urban Runoff

Urban runoff is comprised of many different flow phases. These may include dry-weather base flows, stormwater runoff, combined sewer overflows (CSOs) and snowmelt. The relative magnitude of these discharges vary considerably, based on a number of factors. Season (cold versus warm weather, or dry versus wet weather) and land use have been identified as important factors affecting base flow and stormwater runoff quality.

Land development increases stormwater runoff volumes and pollutant concentrations. Impervious surfaces, such as rooftops, driveways , and roads, reduce infiltration of rainfall and runoff into the ground and degrade runoff quality. The most important hydraulic factors affecting urban runoff volume (and therefore the amount of water available for infiltration) are the quantity of rain and the extent of impervious surfaces directly connected to a stream or a drainage system. Directly connected impervious surfaces include paved streets, driveways, and parking areas draining to curb-and-gutter drainage systems, and roofs draining directly to a storm or combined sewer pipe. Generally, the 5-day biochemical oxygen demand (BOD_5) and nutrient concentrations in stormwater are lower than in raw sanitary wastewater; they are closer in quality to treated sanitary wastewaters. However, urban stormwater has relatively high concentrations of bacteria, as well as high concentrations of many metallic and some organic toxicants.

Table 1 presents older stormwater runoff quality data (APWA, 1969) while Tables 2 and 3 summarize the stormwater data collected as part of the Nationwide Urban Runoff Program (NURP) from approximately 1979 to 1982. The NURP data is the most comprehensive runoff quality data available on a nationwide basis. These two data sets highlight the important effects that land use and source areas (parking areas, rooftops, streets, landscaped areas, etc.) have on stormwater runoff quality.

Table 1. Characteristics of Stormwater Runoff (Source: APWA, 1969)

Location	BOD_5 (mg/L)	Total solids (mg/L)	Susp. solids (mg/L)	Chloride (mg/L)	COD (mg/L)

E. Bay San. Dst., Oakland, CA					
Minimum	3	726	16	300	
Maximum	7,700		4,400	10,260	
Average	87	1,401	613	5,100	
Cincinnati, OH					
Max. season means	12	260			110
Average	17		227		111
LA County Average, 1962-63	161	2,909		199	
Wash., D.C. catch-basin (rain)					
Minimum	6		26	11	
Maximum	625		36,250	160	
Average	126		2,100	42	
Seattle, Washington	10				
Oxney, England	100[a]	2,045			
Moscow, U.S.S.R.	186-285	1,000-3,500[a]			
Leningrad, U.S.S.R.	36	14,541			
Stockholm, Sweden	17-80	30-8,000			18-3,100
Pretoria, South Africa					
Residential	30				29
Business	34				28
Detroit, Michigan	96-234	310-914	102-213[b]		

[a] Maximum [b] Mean

Table 2. Median Stormwater Pollutant Concentrations for All Sites by Land Use (Nationwide Urban Runoff Program, NURP) (Source: EPA, 1983)

Pollutant	Residential		Mixed land use		Commercial		Open/nonurban	
	Median	COV[1]	Median	COV[1]	Median	COV[1]	Median	COV[1]
BOD_5, mg/L	10	0.41	7.8	0.52	9.3	0.31	--	--
COD, mg/L	73	0.55	65	0.58	57	0.39	40	0.78
TSS, mg/L	101	0.96	67	1.14	69	0.85	70	2.92
TKN, µg/L	1900	0.73	1288	0.50	1179	0.43	965	1.00
$NO_2 + NO_3$ (as N) µg/L	736	0.83	558	0.67	572	0.48	543	0.91
Total P, µg/L	383	0.69	163	0.75	201	0.67	121	1.66
Soluble P, µg/L	143	0.46	56	0.75	80	0.71	26	2.11
Total Lead, µg/L	144	0.75	114	1.35	104	0.68	30	1.52
Total Copper, µg/L	33	0.99	27	1.32	29	0.81	--	--
Total Zinc, µg/L	135	0.84	154	0.78	226	1.07	195	0.66

Table 3. Summary of NURP Priority Pollutant Analyses[*] (Source: EPA, 1983)

Pollutant	Frequency of detection (%)	Range of detected concentrations (µg/L)
Pesticides		
α - BHC	20	0.0027 to 0.1
γ - BHC (lindane)	15	0.007 to 0.1
Chlordane	17	0.01 to 10
α - Endosulfan	19	0.008 to 0.2
Metals and cyanide		
Antimony	13	2.6 to 23
Arsenic	52	1 to 51
Beryllium	12	1 to 49
Cadmium	48	0.1 to 14
Chromium	58	1 to 190
Copper	91	1 to 100
Cyanides	23	2 to 300
Lead	94	6 to 460
Mercury	10	0.6 to 1.2
Nickel	43	1 to 182
Selenium	11	2 to 77
Zinc	94	10 to 2400
PCBs and related compounds	None detected in >1% of samples	
Halogenated aliphatics		
Methylene chloride	11	5 to 15
Ethers	None detected in any samples	
Monocyclic aromatics	None detected in >6% of samples	
Phenols and Cresols		
Phenol	14	1 to 13
Pentachlorophenol	19	1 to 115
4-Nitrophenol	10	1 to 37
Phthalate esters		
Bis(2-ethylhexyl)phthalate	22	4 to 62
Polycyclic aromatic hydrocarbons		
Chrysene	10	0.6 to 10
Fluoranthene	16	0.3 to 21
Phenanthrene	12	0.3 to 10
Pyrene	15	0.3 to 16

* Based on 121 samples from 17 cities. This table contains only those compounds found in >10% of outfall samples.

Because some municipalities and water management districts want to use this runoff as a recharge water source for groundwater, there is a need for effective pretreatment of it prior to groundwater recharge (National Academy of Sciences, 1994; Pitt, et al. 1995). Reviews of the research being done on direct infiltration of urban runoff has shown that contamination of groundwater has occurred by infiltration of urban runoff containing the following problem substances:

- Nutrients
- Organics and Pesticides
- Pathogenic Microorganisms
- Metals

- Solids (Suspended and Dissolved)

Nutrients.   Nitrogen- and phosphorus-containing compounds are found in urban runoff primarily from highways. Nitrates result both from vehicular exhaust on the road itself and adjacent soils from fertilization of landscaped areas beside the roads (Hampson, 1986; Schiffer, 1989; German, 1989). Nitrate is very soluble and does not sorb well to soil components during infiltration (Spalding and Kitchen, 1988). Table 2 shows that the highest concentrations of nitrogen-containing compounds, measured both as total Kjeldahl nitrogen (TKN), and nitrite plus nitrate, found in urban runoff in the NURP study was from residential areas. This most likely results from regular fertilization and watering of residential lawns.

Highway runoff also contains phosphorus from motor oils, fertilizers, bird droppings, and animal remains (Hampson, 1986; Schiffer, 1989; German, 1989). Phosphorus tends to sorb to soil components during infiltration, thus preventing phosphorus from reaching the groundwater (Crites, 1985). However, as the sorption sites fill, i.e., the cation exchange capacity of the soil is exceeded, and phosphorus removal decreases (White and Dornbush, 1988).

Organics and Pesticides.   Nationwide testing during NURP did not indicate any significant regional differences in the toxicants detected, or in their concentrations (EPA, 1983). However, land use (especially residential versus industrial areas) has been found to be a significant factor in toxicant concentrations and yields. Concentrations of many urban runoff toxicants have exceeded the EPA water quality criteria for human health protection by large amounts.

Pesticides are used in urban areas for weed and insect control along roadsides, in parks, on golf courses, and on private lawns. Pesticides (α-BHC, γ-BHC, chlordane, and α-Endosulfan) are mostly found in dry-weather flows from residential areas (Pitt and McLean, 1986), and have been related in some locations to the amount of impervious cover and to the distance the runoff must travel before infiltration (Lager 1977; Pruitt, Troutman, and Irwin, 1985; Butler, 1987; German, 1989; Domagalski and Dubrovsky, 1992; Wilson, Osborn, Maida, and Katz, 1990). Pesticides leach to the groundwater when their residence time in soils is less than the time required to filter them or biologically or chemically convert them (Jury, Spencer, and Farmer, 1983).

The appearance of organics in groundwater, like elevated concentrations of nitrates, have been used as an indicator of groundwater contamination in heavily industrial areas (Lloyd, Lerner, Rivett, and Ford, 1988). Most organics are either removed or reduced in concentration during percolation through the soil. Groundwater contamination occurs most readily in areas with pervious soils, such as sand and gravel, and where the distance to the aquifer is small (Troutman, Godsy, Goerlitz, and Ehrlich, 1984). Although organics are also commonly found in stormwater runoff from residential and commercial areas, runoff from industrial areas has been shown to contain higher concentrations of certain organics, such as pentachlorophenol and bis(2-ethylhexyl) phthalate, and the polycyclic aromatic hydrocarbons (chrysene, fluoranthene, phenanthrene, and pyrene) (Pitt and McLean, 1986).

The concentrations of many of these toxic pollutants exceeded the U.S. EPA water quality criteria for human health protection by large amounts. As an example, typical standards for PAHs in surface waters used as drinking water supplies are 0.0028 µg/L (EPA, 1986). As shown in Table 4, urban runoff concentrations of chrysene (0.6 to 10 µg/L), fluoranthene (0.3 to 21 µg/L), phenanthrene (0.3 to 10 µg/L), and pyrene (0.3 to 16 µg/L) (four of the most common PAHs found in urban runoff) have been reported to be from 100 to as much as several thousand times greater than this criteria.

Table 4. Toxic Organic Source Area Observations (Source: Pitt, et al. 1995)

Toxicant	Maximum (µg/L)	Detection freq. (%)	Significant sources
Benzo(a) anthracene	60	12	gasoline, wood preservative
Benzo(b) fluoranthene	226	17	gasoline, motor oils
Benzo(k) fluoranthene	221	17	gasoline, bitumen, oils
Benzo(a) pyrene	300	17	asphalt, gasoline, oils
Fluoranthene	128	23	oils, gasoline, wood preservative
Naphthalene	296	13	coal tar, gasoline, insecticides
Phenanthrene	69	10	oils, gasoline, coal tar
Pyrene	102	19	oils, gasoline, bitumen, coal tar, wood preservative
Chlordane	2.2	13	insecticide
Butyl benzyl phthalate	128	12	plasticizer
Bis(2-chloroethyl) ether	204	14	fumigant, solvents, insecticides, paints, lacquers, varnishes

Bis (2-chloro-isopropyl) ether	217	14	pesticides
1,3-Dichloro-benzene	120	23	pesticides

Pathogenic Microorganisms.   Most bacterial characterization of urban runoff has focused on fecal coliforms, mainly because of their historical use in water quality standards. However, many researchers have concluded that, for many reasons, the fecal coli-form test is not a reliable test for accurately assessing the pathogenicity of recreational waters receiving urban runoff from storm sewers with no known source of contamination. Pathogenic bacteria routinely have been found in urban runoff at many different locations (Pitt, 1983). Historically, fecal coliform limits of less than 200 organisms/100 mL have been recommended because the detection frequency for *Salmonella* has been found to increase sharply in waters receiving sanitary sewer discharges when the fecal coliform number exceeds this standard. The occurrence of *Salmonella* in urban runoff is generally low, with their reported densities ranging between less than one to ten organisms/100 mL when it is detected; however, numerous urban runoff studies have not detected any *Salmonella*. The occurrence of *Salmonella* in urban runoff at these concentrations generally is not considered to be a health hazard because of required infective dose is greater than these concentrations. *Salmonella* observations have not been found to correlate well with fecal coliform observations, illustrating the poor quality of the fecal coliform test for assessing pathogenicity of the runoff (Pitt, 1983).

Urban runoff has also been found to contain other pathogens whose required infective dose is much smaller than that of *Salmonella* or whose mode-of-entry is not ingestion. These pathogens include, but are not limited to, *Pseudomonas aeruginosa*, *Shigella*, or enteroviruses. *Shigella* species causing bacillary dysentery are one of the primary human-enteric-disease-producing bacteria present in water. *Pseudomonas* is reported to be the most abundant pathogenic bacteria organism in urban runoff and streams, with several thousand *Pseudomonas aeruginosa* organisms per 100 mL being common. Relatively small populations of *P. aeruginosa* are reported to be capable of causing water-contact health problems ("swimmers ear" and skin infections), and *P. aeruginosa* is resistant to antibiotics. Pathogenic *E. coli* can also be commonly found in urban runoff (Pitt, 1983).

Viruses also may be important pathogens in urban runoff. Very small viral concentrations are capable of producing infections or diseases, especially when compared to the large numbers of bacteria organisms required for infection. Viruses are usually detected, but at low levels, in urban receiving waters and stormwater (Pitt, 1983).

Infiltration will increase bacterial and viral penetration into the soil profile. Like the organics, the greatest chance for contamination occurs when the distance to the groundwater is small (Boggess, 1975). Most, but not all, pathogens are usually filtered out or inactivated during percolation through the soil (Gerba and Haas, 1988). However, should these pathogens reach the groundwater, they may live there anywhere from several hours to several years, depending on the conditions in the aquifer and on the pathogenic species (Goldschmid, 1974; Crites, 1985; Ku and Simmons, 1986; Wellings, 1988; Jansons, Edmonds, Speight, and Bucens, 1989; Tim and Mostaghim 1991).

Metals.   The heavy metals of most concern in urban runoff are lead, zinc, copper, nickel, and chromium. Most of these heavy metals have very low solubilities at the typical pH of receiving waters. They either are removed by sediment adsorption or are organically complexed with other particulates (Hampson, 1986) and are easily removed during filtration. Metals in urban runoff originate both at industrial sites and on highways, etc., as part of the exhaust and other residue left by vehicular use (Lloyd, et al. 1988). Metals seem to be more prevalent in stormwater runoff from industrial areas, although they are also commonly found in runoff from residential and commercial areas. High concentrations of many of the heavy metals found in industrial area runoff were found both during dry-weather and wet-weather conditions (Pitt and McLean, 1986). Table 5 lists the maximum median and the maximum concentration of several heavy metals in urban runoff, as well as the land use of the area draining to the sampling location.

Table 5. Heavy Metal Source Area Concentrations (Source: Pitt, et al. 1995)

Toxicants	Concentration (µg/L)	Source area
Cadmium		
Maximum	8	Vehicle service area runoff
Max. median	220	Street runoff
Chromium		
Maximum	100	Landscaped area runoff
Max. median	510	Roof runoff

Copper		
Maximum	160	Urban receiving water
Max. median	1250	Street runoff
Lead		
Maximum	75	Combined sewer overflow
Max. median	330	Storage area runoff
Nickel		
Maximum	40	Parking area runoff
Max. median	130	Landscaped area runoff
Zinc		
Maximum	100	Roof runoff
Max. median	1580	Roof runoff

Solids.   Suspended solids are of concern in runoff because of their ability to clog infiltration areas (Crites, 1985) and treatment devices that use filtration. During percolation, the suspended and colloidal particles that were not stopped at the surface travel downward until they are trapped by pores that are smaller than they are. Fine to medium textured soils remove essentially all of the suspended solids by straining, while coarse textured soils allow deeper penetration of these particles (Bouwer, 1985; Treweek, 1985). If the aquifer is close to the surface and the soil does not provide adequate filtration, the suspended particles will enter the aquifer and increase the turbidity of the groundwater.   Dissolved solids are in urban runoff due to the use of salt to de-ice roads in the winter and due to fertilizer and pesticide salts from the use of those items on residential lawns, parks, golf courses, and roadsides (Merkel, Grossman, and Udluft, 1988). Most salts are not removed during percolation through the soil or through a filter media. In fact, the concentration of groundwater tends to increase due to the leaching of salts out of the soils (Nightingale and Bianchi, 1977). In general, once contamination with salts begins, the rapid movement of salts occurs and the concentration does not decrease until the source is removed (Higgins, 1984). *Urban Snowmelt Water Quality*

For many years, emphasis was placed on the study and control of stormwater runoff pollution and other urban runoff sources, such as snowmelt, received little attention. However, a large percentage of the annual runoff in northern climates comes from snowmelt, and in urban areas with seasonal snow cover, snowmelt runoff may contribute significantly to the pollution of streams, lakes and rivers.

The limited studies that are available on snowmelt runoff have shown that the median concentrations of pollutants in snowmelt are not strikingly different from the NURP average concentrations, except for chloride, some solids, and bacteria concentrations. The few studies that have examined both cold weather and warm weather runoff at the same urban outfall have demonstrated that snowmelt runoff contains approximately the same concentrations of pollutants as rain runoff, with the exception of higher dissolved solids concentrations, as chlorides, in the snowmelt due to road salting. In addition, phosphorous concentrations appear to be consistently lower in snowmelt than in urban rainfall runoff. Results from several investigations that examined both warm and cold weather runoff are presented in Table 6.

Bacteria data are not shown in Table 6, but they have been shown to be significantly lower in snowmelt compared to warm weather rainfall runoff. Pitt and McLean (1986) found that fecal coliforms, fecal streptococci, and *Pseuodmonas aeruginosa* populations were significantly lower (by about ten fold) in cold weather runoff compared to warm weather runoff. The Municipality of Anchorage has been studying the bacteriological quality of its surface water resources over several years and also has found that winter coliform measurements are almost exclusively lower than in warm weather runoff (Jokela, 1990).

When it rains on a snowpack, heavy pollutant loads can be produced because both soluble and particulate pollutants are flushed simultaneously both from the snowpack and deposited sediment on the urban surfaces such as roads, parking lots, roofs, and saturated soil surfaces. The intensity of runoff from a rain-on-snow event is usually much greater than during a summer thunderstorm because the ground is saturated or frozen (minimal infiltration), and the rapidly melting snowpack also provides added runoff volume (Oberts, 1994). During monitoring in Toronto, Pitt and McLean (1986) found that rainfall on an existing snowpack contributed over 80% of the total cold weather runoff volume.

Table 6. Comparison of Snowmelt and Rainfall Runoff Quality (concentrations in mg/L)

(Sources: Pitt and McLean, 1986; Daub, Forster, Hermann, Robien, and Striebel, 1994;
Pope and Bevans, 1984; Novotny, 1986; Bennett, Linstedt, Nilsgard, Battaglia, and Pontius, 1981)

Location	Land use	Suspended solids			Dissolved solids			COD			Ref.
		Snow-melt	rain runoff	snow/rain	Snow-melt	rain runoff	snow/rain	snowmelt	rain runoff	snow/rain	
Toronto, Ontario	Residential (median values)	30	22	1.4	1530	230	6.7	40	55	0.7	1
Toronto, Ontario	Industrial (median values)	95	117	0.8	1240	208	6.0	94	106	0.9	1
Bayreuth, Germany	Urban roof & street (range)	39-495	4-296	N/A	N/A	N/A	N/A	N/A	N/A	N/A	2
Topeka, Kansas	Resid. & commer. (median values)	27	362	0.1	1380	232	5.9	34	46	0.7	3
Topeka, Kansas	Agriculture (median values)	10	671	0.02	592	232	2.6	19	40	0.5	3
Milwaukee, Wisconsin	Residential (mean values)	1-398	N/A	N/A	N/A	N/A	N/A	250	38	6.6	4
Milwaukee, Wisconsin	Commercial (mean values)	N/A	N/A	N/A	N/A	N/A	N/A	203	81	2.5	4
Boulder, Colorado	Resid. & commer. (range)	1-1229	24-3730	N/A	N/A	N/A	N/A	8-936	9-1557	N/A	5

Location	Land use	pH			Total Kjeldahl N			Total phosphorus			Ref.
		Snow-melt	rain runoff	Snow/Rain	Snowmelt	rain runoff	snow/rain	snowmelt	rain runoff	snow/rain	
Toronto, Ontario	Residential (median values)	N/A	N/A	N/A	0.17	2.5	0.07	0.23	0.28	0.8	1
Toronto, Ontario	Industrial (median values)	N/A	N/A	N/A	2.5	2.0	1.3	0.50	0.75	0.7	1
Bayreuth, Germany	Urban roof & street (range)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	2
Topeka, Kansas	Resid. & commer. (median values)	N/A	N/A	N/A	1.8	2.1	0.9	0.14	0.36	0.4	3
Topeka, Kansas	Agriculture (median values)	N/A	N/A	N/A	1.5	1.8	0.8	2.0	0.79	2.5	3
Milwaukee, Wisconsin	Resident. (mean values range)	6.7-8.1	N/A	N/A	3.3	2.2	1.5	0.17	0.26	0.6	4
Milwaukee, Wisconsin	Commer. (mean values range)	5.7-8.2	N/A	N/A	3.3	1.9	1.7	0.20	0.28	0.7	4
Boulder, Colorado	Resid. & commer. (range)	N/A	N/A	N/A	0.22 -5.4	1.7- 3.7	N/A	0.6- 3.3	0.2-7	N/A	5

Table 6. (Continued)

Location	Land use	Copper			Lead			Zinc			Ref.
		snow-melt	rain runoff	snow/rain	snow-melt	rain runoff	snow/rain	snow-melt	rain runoff	snow/rain	
Toronto, Ontario	Resident. (median values)	0.04	0.03	1.3	0.09	0.06	1.5	0.12	0.06	2.0	1
Toronto, Ontario	Industrial (median values)	0.07	0.06	1.2	0.08	0.08	1.0	0.31	0.19	1.6	1
Bayreuth, Germany	Urban roof & street (range)	0.03- 0.15	0.01- 0.11	N/A	0.02- 0.16	0.005 -0.14	N/A	0.24- 1.18	0.07- 1.17	N/A	2

Topeka, KS	Resid. & commer. (median values)	0.005	0.02	0.3	0.035	0.07	0.5	0.055	0.11	0.5	3
Topeka, KS	Agriculture (median values)	0.01	0.02	0.5	N/A	0.02	N/A	0.01	0.06	0.2	3
Milwaukee, WI	Resident (median values)	N/A	N/A	N/A	0.12	0.12	N/A	N/A	N/A	N/A	4
Milwaukee, WI	Commercial (median values)	N/A	N/A	N/A	0.27	0.52	N/A	N/A	N/A	N/A	4
Boulder, CO	Resid. & commer. (range)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	5

Reference 1. Pitt and McLean 1986.
Reference 2. Daub, et al. 1994.
Reference 3. Pope and Bevans 1984.
Reference 4. Novotny, 1986.

Reference 5. Bennett, et al. 1981.

Much of the high dissolved solids concentrations in snowmelt can be attributed to high chloride levels. Year-round monitoring of pollutants has been conducted at the Monroe Street detention pond in Madison, WI, from 1986 to 1988 (House, Waschbusch, and Hughes, 1993). Chloride levels were found to decrease dramatically between February and April. February runoff samples typically contained 1,000 to 3,000 mg/L chloride, but decreased to less than 100 mg/L by the end of April. Snowmelt chloride concentrations during the next winter rose again to over 1,000 mg/L.

Pollutant Concentrations in Snowmelt Sheetflows.   Pitt and McLean (1986), during analysis of snowmelt sheetflows from residential and urban catchments in Toronto, found that, in general, source areas contribute similar quality water during both rain and snowmelt events. For example, the highest concentrations of lead and zinc in both snowmelt and rainfall runoff were found in samples collected from paved areas and roads.

Fecal coliforms and suspended solids, however, showed significant differences between snowmelt and rainfall runoff. Fecal coliform counts were significantly higher on sidewalks and on, or near, roads during snowmelt periods compared to warm weather periods, even though the outfall fecal coliform counts during the winter were much less than during warm weather. It is likely that dogs, and hence their feces, stayed in areas that were generally free of snow. In warm weather, dogs would be less likely to be restricted to these areas. Cold weather sheetflow median suspended solids concentrations in grass and open areas (80 mg/L) were much less than the concentrations observed during warm weather runoff (250 mg/L). Total solids in snowmelt sheetflows in grass or bare open areas also were reduced dramatically compared to warm weather runoff, probably because snowmelt has significantly less erosion energy than rain. Grass and open areas generally are located relatively far from the drainage system and particles from these areas likely are not easily transported long distances during periods of low energy. In contrast to the grass and open areas, total solids concentrations were greater during snowmelt periods in road sheetflow samples, likely due to the large amount of road sanding debris and high chlorides near roads that was relatively easy to transport in the gutter and drain systems.

Roadways generally contributed the most pollutants (yields and concentrations) to snowmelt runoff. Pitt and McLean (1986) analyzed snow samples along a snowpack transect perpendicular to a road. These data showed that the pollutant levels dropped dramatically at greater distances from the roadway. At distances greater than about 3 to 5 meters from the edge of the roadway, the snowpack pollutant concentrations were relatively constant.

Snowmelt Quality Summary.   The following conclusions were obtained after reviewing numerous studies that have investigated urban snowmelt quality:

- Urban snowmelt runoff quality is similar in nature to stormwater runoff quality from the same source area, except for dissolved solids and chlorides (much higher), and bacteria (much lower).

- The high dissolved solids concentrations in snowmelt result from the high chloride quantities used in road salting.

- Atmospheric scavenging of air pollutants by snowflakes is the source of only a small fraction of the snowmelt pollutants.

- Most of the contamination of snow occurs after it is on the ground. Snow becomes polluted while it accumulates for long periods in snowpacks. Snowmelt runoff picks up few pollutants as it flows over the various urban surfaces. However, rainfall on an existing snowpack causes most of the snowpack related discharges.

- Roads, parking lots and storage areas are important pollutant sources in all land uses during snowmelt periods. In residential areas, yards and open areas are also major sources of nutrients.

Filterable Fraction of Stormwater Pollutants

Table 7 summarizes the filterable fraction of toxicants found in   stormwater runoff sheet flows from many urban areas (Pitt, et al. 1995). Pollutants that occur mostly in a filterable form have a greater potential of affecting the groundwater and are more difficult to control using conventional stormwater control practices, sedimentation and sand filtration. Fortunately, most of the toxic organics and metals are associated with the non-filterable fraction (suspended solids) of the runoff. However, probable exceptions to this rule include zinc, fluoranthene, pyrene, and 1,3-dichlorobenzene. In general, dry weather flows in storm drainage systems tend to have much higher concentrations of the toxicants in the filterable fraction.Table 7. Reported Filterable Fractions of Stormwater Toxicants (Source: Pitt, et al. 1995)

Constituent	Filterable Fraction (%)
Cadmium	20 to 50
Chromium	<10
Copper	<20
Iron	small amount
Lead	<20
Nickel	small amount
Zinc	>50
Benzo (a) anthracene	none found in filtered fraction
Fluoranthene	65
Naphthalene	25
Phenanthrene	none found in filtered fraction
Pyrene	95
Chlordane	none found in filtered fraction
Butyl benzyl phthalate	irregular
Bis (2-chloroethyl) ether	irregular
Bis (2-chlrorisopropyl) ether	none found in filtered fraction
1,3-dichlorobenzene	75

Sources of Stormwater Pollutants

High bacteria populations have been found in sidewalk, road, and some bare ground sheetflow samples collected from locations where dogs would most likely be "walked." Tables 4 and 5 summarize toxicant concentrations and likely sources or locations having some of the highest concentrations detected (Pitt, et al. 1995). The detection frequencies for the heavy metals are all close to 100 percent for all source areas, while the detection frequencies for the organics shown ranged from about 10 to 25 percent. Vehicle service areas had the greatest abundance of observed organics, with landscaped areas having many of the observed organics. Residential source areas can contribute a significant variety of toxic metals and organics to the runoff, as is shown in Table 8. However, because the contribution of any single residence is generally small and typically does not have the variety of chemicals listed in Table 8, attempting to treat the runoff from residential source areas on a residence-by-residence basis is not feasible.

One reason that many of the chemicals listed in Table 8 and in prior tables do not vary much between the land use groups is that a major contributor to baseline pollution in any urban runoff is atmospheric deposition of airborne pollutants. Airborne pollutants land indiscriminately in a watershed and where they land is determined by the dispersion ability of the wind and the nature of the pollutants at the time of discharge into the atmosphere. The runoff from a watershed then is a combination of the atmospheric deposition baseline across the watershed (independent of land use) and on the pollutant release from individual locations in the watershed. It is these additional pollutant loadings that are related to land use and are of particular concern.

Based upon a review of the data collected both during the NURP program and by other stormwater researchers, the control of small critical area contributions to urban runoff ('hotspots') may be the more cost- effective approach for treatment/reduction of stormwater toxicants. The general features of the critical source areas appear to be large paved areas, heavy vehicular traffic or areas with many vehicular starts, and the outdoor use and/or storage of problem pollutants. Using these general guidelines, the problem point source areas identified for this work are industrial manufacturing facilities, service stations, vehicle maintenance facilities, and some other commercial developments. Residential runoff is relatively innocuous and is well below the national average concentration in runoff for most hydrocarbons, metals and priority pollutants, although it is a major contributor of several conventional stormwater pollutants including solids/sediment, total phosphorus, and bacteria. Residential runoff usually is not a problem in a watershed because residential areas contribute smaller unit area volumes of runoff and because the runoff concentration is relatively low.

Table 8. Urban Runoff Hazardous and Toxic Substances*
(Sources: Galvin and Moore, 1982; EPA, 1983; Pitt and McLean, 1986)

Residential Areas	Industrial Areas
Bis(2-Ethylene)phthalate	1,2-Dichloroethene
Phenol	Methylene Chloride
Butylbenzyl phthalate	Tetrachloroethylene
Di-N-butyl phthalate	Butylbenzylphthalate
Benzene	Di-N-butyl phthalate
BHC	Phenanthrene
Chlordane	Pyrene
Dieldrin	Benzene
Endosulfan Sulfate	Chloroform
Endrin	Ethylbenzene
Isophorone	n-Nitrosodimethylamine
Methoxychlor	Toluene
Pentachlorophenol	PCB-1254
Aluminum	PCB-1260
Copper	Pentachlorophenol
Lead	Phenol
Zinc	Aluminum
Cadmium	Chromium
Other Heavy Metals	Lead
	Other Heavy Metals

* Substances found in ≥10% of stormwater analyzed.

Stormwater Runoff Treatment Media

Most stormwater treatment devices currently in use or in development use sedimentation as their primary pollutant removal mechanism since most of the pollutants in runoff are associated with the particulates. Filtration may also be used as a second step because the contaminated particulates are strained out as the water passes through the filter bed and either are trapped on the surface of the filter or among the media's pores. Filtration is very effective, as it can achieve 90% removal of particles between 6 and 41 μm. However, filtration/straining alone cannot remove soluble pollutants (Pitt, et al. 1995; Claytor and Schueler, 1996). Several comparisons have been done between filtration and other devices for stormwater runoff treatment. The first comparison is to look at the feasibility of each type of treatment device. The results are given in Table 9. The comparison of pollutant removal capabilities is given in Table 10.

Table 9. Stormwater Treatment Device Characteristics
(Source: Claytor and Schueler, 1996)

Criteria	Ponds	Wetlands	Infiltration	Filters
Soils	Most	Most	Soil-dependent	All
Drainage area	10 Acres min.	10 Acre min.	2-5 Acre max.	2-5 Acre max.
Head	0.9-1.8 m	0.3-1.8 m	0.6-1.2 m	0.3-2.4 m
Space	2-3% Site	3-5% Site	2-3% Site	2-7% Site
Cost/Acre	Low	Moderate	High	Mod-High
Water Table	No Restrictions	No Restrictions	1.2 m below	0.6 m below
Cleanout	2-10 yrs.	2-5 yrs.	1-2 yrs.	1-3 yrs.
Life	20-50 yrs.	20-50 yrs.	1-5 yrs.	5-20 yrs. (est.)

Table 10. Runoff Treatment Pollutant Removal Capabilities
(Source: Claytor and Schueler, 1996)

Pollutant	Ponds	Wetlands	Infiltration	Filters
Sediment	Excellent	Excellent	Excellent	Excellent
Phosphorus	High	High	Excellent	Fair-High
Nitrogen	Fair	Fair	High	Fair
Soluble Nutrients	High	Fair	High	Low
Bacteria	Low-High	unknown	unknown	Low-High
Hydrocarbons	High	High	unknown	Excellent
Trace Metals	Fair	Fair-Excellent	High	Fair-Excellent

Low: 0-25% removal   *Fair*: 26-50% removal   *High*: 51-75% removal
Excellent: 76% + removal

Filtration can be defined as an interaction between a suspension and a filtering material (Ives, 1990). Pollutants are removed from the solution when they become attached to the media or to previously captured particles. In general, the three key properties of a filter are surface area, depth and profile, and filter performance is measured by effluent water quality (traditionally, turbidity and suspended solids concentration, possibly particle counts and dissolved organic carbon concentration [DOC]), water production (unit filter run volume), and head-loss development (rate and time to back wash), all of which change over time (Clark, Lawler, and Cushing, 1992; Tobiason, Johnson, Westerhoff, and Vigneswaran, 1993). Surface area loading is usually given as the percentage of the total impervious area draining to the filter, compared to the filter surface area. The filters examined during this research would require about 1% of the impervious drainage area. The surface area required for any filter depends upon both the media type and the rainfall patterns for the area. The depth of the media is also important with stormwater filter depths usually ranging between eighteen inches and four feet. The shallow bed depths are typically used for both hydraulic and cost reasons because less filtering time and less media are required in a shallow bed. However, the tradeoff for a shallow filter depth usually is effluent quality, i.e., the shallower the filter, the less removal that is likely to occur. In general, filtering systems should be sized using the volume of runoff to be filtered and the filtering media selected based upon the pollutants of interest.

The performance of filters that are also adsorbers or ion-exchangers is measured by the change in concentration of the constituents of interest as a result of filtration. Filtration performance depends on the source water quality (types and concentration of natural organic matter and suspended particles), any required chemical additions and mixing processes, and physical characteristics of the media (type, size distribution, depth, and hydraulic loading rate) (Tobiason, et al. 1993). Although not likely to be significant for most stormwater filters, two fluid properties that can affect filtration are viscosity and density. Density and viscosity are both temperature dependent, and density will also depend upon the concentration of dissolved solids in the water (Clark, 1990). In stormwater runoff treatment, viscosity variations in the runoff between areas is insignificant because the water would be either ice or steam before the viscosity change would affect the filter's performance. Density changes may have a larger effect on filtration of runoff because it is also dependent upon the dissolved solids concentration. This effect, however, is likely to be noticeable for filters receiving snowmelt runoff. In general, the biggest control on a filter's overall performance is the concentration of previously deposited particles (Tobiason, et al. 1993).

Properties of the media that can affect filtration performance include straining ability, adsorption/ion-exchange ability, available microbial action, and plant resistance and uptake. These last two properties are usually only important in stormwater filters which have a steady water supply and a thriving, but well-maintained, plant cover. For other filters, only the first two properties are of interest in filtration design. The chemical properties of media that are good ion-exchange or adsorption resins include a high organic content or clay, a high cation exchange capacity (CEC), and a neutral to alkaline pH. Pure sand has minimal adsorption capacity; however, once the filter ages and a biofilm covers the sand grains, the sand filter is capable of excellent adsorption when the pH conditions are in the correct range. This pH dependence is also present in the organic media of interest.

Microbial action is very important in many filtration processes. It used to be believed that stormwater filters dried out between storms when the interevent dry period was several days and that this drying of the media would prevent the formation of an effective microbial colony. Research has shown, however, that the media (especially the organic media) do not dry out between storms, and a microbial colony is established in areas of the filter where there is a sufficient organic carbon source. Two of the more important microbial processes in filtration are nitrification and denitrification. Nitrification converts organic nitrogen to ammonia and the ammonia to nitrite followed by nitrate. Denitrification converts the nitrate to nitrogen gas, which is released to the atmosphere. Research on stormwater filters currently in use indicates that significant nitrification is occurring in the filters, and the concentration of nitrate in the effluent is greater than it was in the influent. Denitrification pockets have been located in some of the stormwater filters; however, denitrification does not occur to a sufficient degree. Because of the concern over nutrients entering surface waters, some new filters are being constructed to provide a zone of denitrification. The ability to denitrify to an appreciable extent requires that a filter section be anaerobic. This is usually done by providing a saturated zone at the bottom of the filter, where several inches of gravel remain submerged, even when the rest of the filter dries out. In order to keep the filter working appropriately (most other beneficial microbial action requires an aerobic environment), the submerged area should be separated from the rest of the filter by several inches of dry gravel (Claytor and Schueler, 1996).

CHAPTER 2 - LITERATURE REVIEW: SAND

The use of sand filtration is common throughout the United States. Water supply treatment plants have successfully used sand filtration for many years. Wastewater treatment plants often use sand filtration to polish their effluent before release, especially as the regulatory requirements for the discharge of suspended solids becomes more stringent. Sand filters are also popular as stormwater runoff treatment, especially in urban areas where the filters must be retrofitted and property values decree that the filters be located underground (Claytor and Schueler, 1996).

Physical Characteristics

Slow sand filters are characterized by slow filtration rates, an extremely narrow range of sand particle sizes, the lack of chemical pretreatment, relatively long filter runs between cleanings, and surface scraping and sand removal instead of backwashing as a cleaning technique (Collins, Eighmy, Fenstermacher, and Spanos, 1992). Filtration rates are as much as fifty times slower than those of rapid sand filters; consequently, slow sand filters require significantly more surface area in order to filter comparable volumes of water (Crittenden, Vaitheeswaran, Hand, Howe, Aieta, Tate, McGuire, and Davis, 1993). Slow sand filter media is characterized by certain parameters: size distribution, settling velocity, porosity, grain integrity, shape, hardness (resistance to attrition), and the results of visual and microscopic examinations (Ives, 1990). Slow sand filters need to have a minimum vertical distance (or fall) of at least 0.6 m, but preferably 1.5 m, from inflow to outflow to drive the water by gravity through the entire filter (Claytor and Schueler, 1996).

Fine sand/silt filters remove particulates by direct straining on the surface of the filter media. The combination of grain size and bed depth will determine the effectiveness of the filter. Naghavi and Malone (1986) demonstrated that the combination of grain size (0.2 mm) and a shallow bed depth produced an average fluorescence removal of approximately 97%, even with no chemical pretreatment. This combination also had the highest initial filtration rate ($226 \ m^3 \ m^{-2} \ day^{-1}$) and a lower initial headloss (7.3 cm). The effect of media size on filtering ability also was demonstrated by Tobiason, et al. (1993) in a 2.5 cm inner diameter (ID) acrylic column filled with 17 cm of 0.4 mm glass-bead filter with the test suspensions that contained either one size or a mixture of 0.27, 1.3 and 10 μm diameter particles. Smaller particles affected the rate of removal of larger particles and the rate of head-loss development. Head-loss development was typically linear with time, and, for suspensions of mixed particle sizes, it generally was the same as, or somewhat lower than, head loss for monodisperse suspensions of the smaller-sized particle (Tobiason, et al. 1993). Head loss (or hydraulic resistance) is determined by the filter's surface area, which depends on the size and number of grains, not the grains' weight. In order to have the same head loss development pattern in a 'single-size' media filter, the new filter would require a diameter equal to the

d_{10} of the mixed-size media (Ives 1990). Head loss results from increased fluid drag, pore constriction, and increased interstitial velocities caused by particle deposition. Small particles cause more head loss because of their high surface area per unit volume (Tobiason, et al. 1993). Head loss is spread more evenly through the filter in media with larger particle diameters. Therefore, capturing a particle with a larger media results in less head loss than capturing it with smaller media (Clark, et al. 1992)

Removal is different at the various depths of the filter, with the influent particle concentration being reduced dramatically in the top section of the filter and smaller reductions occurring near the bottom of the filter. This effect is most pronounced for filters with smaller sand sizes; therefore, removal efficiency in the larger media improves substantially compared to the smaller media at each successive depth of the filter. Later in the filter run, large particles apparently are less effectively removed in the top section of the filter, suggesting that small particles entered the filter and were captured by previously retained particles, thereby forming a floc on the media surface. If the flocs break off the surface, they may pass unhindered through the filter media and be measured as larger particles. In addition, particles with surface chemistry favorable for retention in the medium likely are captured in the top section of the filter while the particles with unfavorable surface chemistry reach the lower section where they still are not removed from solution (Clark, et al. 1992). Percent removal is a function of both sand depth and particle size and for a given removal efficiency; using coarse sand and a deep bed is recommended by Farooq and Al-Yousef (1993) because this type bed will require less cleaning than the corresponding fine sand in a shallow bed filter.

Filtration velocity, to a lesser extent than media size, affects removal efficiency, bed depth use, and head loss. Head loss is directly proportional to velocity in new filters, but for ripened filter beds, the direct proportionality does not apply. Increased velocity pushes particles deeper into the filter bed prior to capture, thus allowing more of the filter depth to be used in particle capture. This leads to reduced head loss and, therefore, larger quantities of water can be treated before cleaning is necessary (Clark, et al. 1992). There is an upper limit on filtration velocity, however. At rates higher than 5 m/day of sanitary wastewater, the sand filter clogs within a few days while for rates less than 1 m/day, collected organic particles decompose in the filter and free up pore space, and the run length is quadrupled (Fujii, Somiya, and Takeda, 1987).

For sand, as for other filter media, the shape of the curve of percent captured versus particle diameter depends on the particle capture mechanism, the filter medium, the fluid being filtered, and the filtration conditions (Shucosky, 1987). Generally, dissolved oxygen concentrations and pH decrease in sand filtration. Particulate chemical oxygen demand (COD), particulate organic nitrogen, and particulate phosphorus are removed during filtration, even before the filter is ripened. However, very little of the soluble fractions of the above constituents was removed (Fujii, et al. 1987).

Using lateral viewing endoscopes, unexpected phenomena, such as tumbling grain motion and void formation ('wormholes,' or pores larger than a sand particle's diameter), have been observed in traditional sand filters, especially rapid filters or those using countercurrent filtration. These 'wormholes' start with holes in the surface deposit and remain open despite the continuing flow of solids into them. Aggregates, especially those of weakly-bound compounds, that enter the wormholes, even if they are larger than the hole, may be deformed or disrupted by the hole, yet they do not completely stop flow through the hole. This aggregate 'destruction' during filtration only occurs to an appreciable extent when substantial deposits are present (Ives, 1989). Preferential flow (macropore, fingering, or funneled flow) also has been observed in sand filters, as it has in many other filters and soils. During preferential flow, the fluid follows the local wetting front in wormholes and bypasses the matrix pore space. Filtration efficiency for preferential flow pathways is much smaller than it is for matrix pore flow because flow through preferential pathways is more rapid and less time is available for straining and/or sorption (Steenhuis, Staubita, Andreini, Surface, Richard, Paulsen, Pickering, Hagerman, and Geohring, 1980).

General Removal Capabilities

Slow sand filters are extremely effective in removing suspended particles, and effluent turbidities are consistently below 1.0 NTU. Bacteria, viruses and *Giardia* cysts are also removed with enhanced removals once a bacterial population is established on the filter. However, sand filters have only a limited ability to remove organic material that are precursors to trihalomethane formation and the biodegradable fraction of dissolved organic carbon (BDOC) (Collins, et al. 1992; Eighmy, Collins, Spanos, and Fenstermacher, 1992; Farooq and Al-Yousef, 1993). Stratified sand filters have been shown to remove enteric viruses, along with total organic carbon (TOC) from septic tank effluent at a loading rate of 0.061m/day, even from sand filters that contained new sand, i.e., had no schmutzdecke and, therefore, no bacterial breakdown of pollutants (Gross and Mitchell, 1990). A sand filter with an effective sand size of 0.23 mm and a loading rate of 3.84 m/day was shown to effectively remove biochemical oxygen demand (BOD) (86%), suspended solids (68%), turbidity (88%), and total coliform bacteria (99%) from sanitary wastewater (Farooq and Al-Yousef, 1993). High algae removal can be accomplished using media with median sand sizes ≤ 0.2 mm (Naghavi and Malone, 1986). Sand filtration at a Superfund site showed suspended solids removal of about 50% for waters that contained mostly colloidal-sized particles and 80% to 100% removal for waters whose solids were larger. One unexpected result for the filtration was that solids breakthrough occurred much earlier than expected, possibly because the filter was not in

continuous operation (Dahab, Becker, and Riley, 1991). The presence of wormholes was not investigated by Dahab, et al. (1991) although this is one potential explanation for the early breakthrough.

Sand filtration, without modification of the sand by ripening or by adding a surface coating of an adsorber such as manganese or ferric oxide, is not effective at removing dissolved constituents. Deethylatrazine was consistently detected in the effluent of one sand filter (2 cm ID x 30 cm long filter) used to treat a natural groundwater spiked with 200 µg/L of atrazine (applied at 5 mL/min for 70 days; 23 m^3 m^{-2} day^{-1}) until the filter ripened (Selim and Wang, 1994). Sand filtration also does not remove total suspended solids (TSS) from pulp and paper mill secondary effluent as effectively as it does from municipal secondary effluent, likely because the nature and size of the solids are considerably different (unimodal at 2 µm) from the nature and size of the organisms filtered from secondary wastewater (bimodal at 4 and 85 µm). The pulp and paper mill effluent had mostly very small particles, the range where the sand filter is not as effective (Biskner, Baron, and Millcan, 1978).

Ripening of the Sand Filter

Ripening is the development of a bacterial biofilm, the 'schmutzdecke,' on the sand filter which improves the removal ability of the filter. This increased efficiency occurs for all particle sizes initially, but eventually only continues for small sizes with the removal efficiency decreasing and possibly becoming negative for larger particles. Captured particles aid in the collection of subsequent particles by partially blocking and restricting passage through the pores. Therefore, the rate of increase in particle removal efficiency depends on the influent particle concentration. When more time elapses between collisions of particles on the media surface and those in solution, the first collected particle may migrate to the bottom of the grain and greatly reduce the opportunity for interaction with the next incoming particle. Thus, the removal efficiency is greater and ripening is quicker when the influent concentration is greater (Clark, et al. 1992).

Submicron particles also improve the deposition of larger particles because they increase the apparent surface roughness of the media and/or the large particle (Tobiason, et al. 1993). Ripening of the filter creates rougher pore channels, which slows down the flow and provides more contact time between the media and the pollutants in the water (Fujii, et al. 1987). In addition, larger particles may hinder the initial deposition of the smaller particles because of unfavorable hydrodynamic interactions or differences in destabilization (Tobiason, et al. 1993).

Sand filters have a more limited capacity for substrate growth and thus have a smaller microbial population, as compared to organic media filters of the same size (Selim and Wang 1994). Even when ripening is complete, head-loss development is approximately linear with time (or mass deposited) (Tobiason, et al. 1993).

Adsorbent Coatings

Another technique for improving the removal efficiency of a sand filter is by adding an adsorbent coating, usually an iron or manganese oxide, to the sand grains, thus providing adsorption sites for the ions in solution. Potential sorption mechanisms include diffusion into the lattice of the minerals; adsorbing at sites on the sand surface; adsorbing sites on hydrous iron and manganese oxides and hydroxides; and complexing at sites on natural organic matter in the schmutzdecke. The iron oxide coating on sandy soil has been found to bind metals of all sizes very strongly. Metal binding strength is relatively low in the exchangeable fraction and increases in the non-exchangeable fraction because metals in the non-exchangeable fraction likely are incorporated within the crystalline lattice or strongly sorbed to the mineral surface. The non-exchangeable fraction, therefore, is 'permanently bound' to the sand under normal operating conditions. The non-exchangeable fraction also contains the greatest concentration of sorbed metals, except zinc. The smallest sized media have the greatest mass concentration of metals. Lead binds more strongly to the smaller particles while arsenic, copper, and zinc show similar affinities for all size fractions. Metal sorption kinetics show the existence of both a fast reaction, where metals bind to surface sites, and a slow reaction, where metals bind to interior sites. Reaction kinetics also affect the availability of metals for sorption. Metals from the dissolution of the soluble compounds are available more quickly for sorption while metals in precipitates or other covalently bonded compounds are not (Van Benschoten, Reed, Matsumoto, and McGarvey, 1994).

Manganese oxide coatings can remove manganese(II) from solution with the rate of sorption being positively correlated to the number of available surface adsorption sites. Chlorine in the manganese(II)-containing influent will oxidize the adsorbed manganese(II) and, therefore, continually regenerate the filter. Removal efficiency is a function of the surface MnO_x(s) concentration, its oxidation state, and the influent pH. Manganese(II) sorption capacity is greater, and the reaction rate is faster when the influent pH is raised (reducing

H^+ ion competition for sites). For a given pH, sorption capacity also is increased as the surface $MnO_x(s)$ concentration is increased. Efficient manganese(II) sorption was found even during the winter when the sorption rates likely are significantly slower. Further research has shown that the coatings do not affect the filter hydraulics either during a run or during cleaning, the clean-bed head loss of the filter, or the effective size and density of the filter media (Knocke, Occiano, and Hungate, 1991).

Limitations

Slow sand filtration has the following limitations and concerns: (1) a limited acceptable range of influents (usually less than two hundred milligrams per liter influent total suspended solids [TSS]); (2) a limited ability to remove organic precursor materials because of a lack of sorption surfaces; and (3) extensive filter downtimes and ripening periods (Collins, et al. 1992).

Cleaning and re-ripening a slow sand filter is difficult and time-consuming; however, several techniques have been developed to "speed up" that process. Wet harrowing in West Hartford, CT, removed the surface mat yet kept the biomass in the filter media down to the depth of harrowing (Eighmy, et al. 1992). Nonwoven, synthetic fabrics have been placed on the sand surface. The fabric has a greater porosity and specific area and is a more efficient filter for larger particles. The benefits of filter mats/fabrics placed on top of the sand surface are longer run times and simpler cleaning that requires only the removal and cleaning of the fabric. However, a filter cover does not improve the ability of a sand filter to treat raw waters of varying quality, and no suitable cleaning method exists for the fabrics in large-scale installations (Collins, et al. 1992).

Stormwater Runoff Treatment

Sand filtration for stormwater treatment began on a large scale in Austin, TX. The Austin sand filters are used both for single sites and for drainage areas less than fifty acres. The filters are designed to hold and treat the first one-half inch of runoff with very good pollutant removal ability.

According to the City of Austin design guidelines, the minimum sand depth should be eighteen inches. These filters may have either gravel, a geotextile, or other fabric on top of the sand to prevent premature clogging with large particles. For a filter built according to Austin's design guidelines, the assumed pollutant removal efficiencies, which are based upon the preliminary results of the City's stormwater monitoring program, are given in Table 11.

In Washington, D.C., sand filters are used both to improve water quality and to slow the runoff in order to prevent large slug inputs to the combined sewer system (CSO). Water quality filters are designed to retain and treat three-tenths to one-half inch of runoff with the exact design based upon the amount of impervious area in the watershed (Shaver, 1994).

In Delaware, the sand filter is an acceptable method for achieving the 80% suspended solids reduction requirement. These filters are intended for sites which have impervious areas that will drain directly to the filter, such as fast-food restaurants and gas stations. In many areas, sand filters precede an infiltration device in order to prevent or postpone clogging of the infiltration device. Sand filters are also used on sites where there is no space to retrofit other infiltration devices (Shaver, 1994).

According to Delaware's guidelines, the sand filter can be expected to adequately remove particulates (TSS removal efficiency 75 - 85 %) but not soluble compounds. Studies of a six-year old sand filter in Maryland that was installed at the drain of a heavily-used parking lot showed that the filter is now becoming clogged. Inspection of the sand below the filter surface has shown that oil, grease, and finer sediments have migrated into the filter, but only to a depth of approximately two to three inches (Shaver, 1994; Galli, 1990).

The sand filter used in Delaware has a similar design to the Austin filters with an eighteen-inch sand depth and a six-inch gravel underdrain. Each filter has a minimum of six to twelve inches of ponding depth/storage head available on top of the filter. Monitoring of a Delaware sand filter which treats the runoff from a 0.28 ha (0.7 acre) section of a parking lot near National Airport in Alexandria, VA, showed that the filter had an average 72% removal of total phosphorus, >80% removal of total suspended solids (influent concentration = 50 mg/L), and >90% removal of zinc (200-630 µg/L influent concentration). The sand filter, which had an underdrain layer, continued to function during freezing weather. Anaerobic conditions will develop in sand filters unless the bottom of the filter is exposed to air. Anaerobic conditions enhance nitrate removal by denitrification but reduce total phosphorus removal because the iron phosphates degrade and release phosphorus (Galli, 1990).

Table 11. Pollutant Removal Efficiencies for Sand Filters

(Source: City of Austin, 1988)

Pollutant	Removal Efficiency (%)

Fecal Coliform Bacteria	76
Total Suspended Solids (TSS)	70
Total Nitrogen	21
Total Kjeldahl Nitrogen	46
Nitrate - Nitrogen	0
Total Phosphorus	33
Biochemical Oxygen Demand (BOD)	70
Total Organic Carbon	48
Iron	45
Lead	45
Zinc	45

Monitoring of a Delaware sand filter at the Alaska Marine Terminal in Seattle showed >80% removal of total petroleum hydrocarbons (TPH) when influent concentrations were 1.2 mg/L and >90% removal of TPH when influent concentrations were 3.1 mg/L. Suspended solids and phosphorus removals were similar to those noted at the National Airport in Alexandria, VA (Galli, 1990).

Herrera Environmental Consultants (1991 and 1995) also have evaluated sand filters as a media for stormwater treatment. Their results indicate that sand filters by themselves are the least effective at removing both total phosphorus (0 to 28 percent removal) and soluble phosphorus (0 to 38 percent removal). Iron sand and sand amended with other constituents, such as calcitic lime and hypnum peat, were found to remove significantly more total phosphorus and soluble phosphorus than sand alone. The sand/calcitic lime mixture removed between 29 and 79 percent of the total phosphorus and between 25 and 93 percent of the soluble reactive phosphorus. The sand/hypnum peat mixture removed between 31 and 94 percent of the total phosphorus and 36 to 99 percent of the soluble reactive phosphorus (Herrera Environmental Consultants, 1991). The addition of steel wool to the sand filter as an adsorbent showed that it was also an effective sorbent media for total and soluble phosphorus removal. Phosphorus removal occurs because the steel wool oxidizes in the presence of water and oxygen and the oxidized iron easily reacts with the phosphate in solution (Herrera Environmental Consultants, 1995).

CHAPTER 3 - LITERATURE REVIEW: ACTIVATED CARBON

Activated carbon separation has long been used in the water treatment and chemical process industries and in hazardous waste cleanup as an effective method for removing trace organics from a liquid. Activated carbon is made first by charring materials such as almond, coconut and walnut hulls, other woods or coal. The char particles are activated by exposing them to an oxidizing gas at high temperatures. The activation process makes the particles porous which creates a large internal surface area available for adsorption (Metcalf and Eddy, 1991).

Organic Removal Capability

Activated carbon has been used for more than fifty years in drinking water treatment plants to remove taste- and odor-causing compounds, along with most synthetic organic chemicals, pesticides, herbicides, color, and trihalomethane precursors (Rael, et al. 1995). Disinfection by-products, including the trihalomethane precursors, have also been removed from drinking water by granular activated carbon (GAC) (Crittenden, et al. 1993; Abuzald and Nakhla, 1994).

Slow GAC filters achieve excellent organic removals (> 90 percent), with the removal efficiency limited by the depth of the filter. This dependence is due to 'slowness' of the transport kinetics and attachment mechanisms inherent in activated carbon sorption. The problem with activated carbon is its exponenential head loss curve, *i.e.*, increasing removal increases head loss development rates, and, therefore, the filters must be cleaned more frequently (Collins, et al. 1992).

Anaerobic charcoal chip reactors, along with anaerobic sand packed reactors, can remove up to 80% of the chemical oxygen demand (COD) at an organic loading rate of 7 kg COD/m^3-d and 60% at 12 kg COD/m^3-d and were able to withstand a shock loading of over 22 kg COD/m^3-d. However, efficiency dropped when wastewaters contained a high

concentration of SO_4^{2-} and Na^+. In general, the removal efficiency of COD is inversely related to loading rates, and no clogging was observed even after one year of operation (Chin, 1989).

Granular activated carbon (GAC) is useful for treating wastewaters with inhibitory, yet adsorbable, compounds that make conventional biological treatment difficult or impossible (Fox, Suidan, Pfeffer, and Bandy, 1990). Activated carbon can remove both dissolved and synthetic organic carbon (DOC and SOC, respectively) compounds from solution. However, provided that adequate contact time exists in the treatment system, equilibrium capacity of the carbon decreases with decreasing initial DOC or SOC concentration. The SOC adsorption rate onto activated carbon decreases with decreasing initial SOC concentration due to competition by natural organic matter. Equilibrium is achieved after three hours with an initial concentration of 109 µg/L trichlorophenol, yet equilibrium takes twenty-four hours when the initial concentration is 34 µg/L trichlorophenol (Najm, Snoeyink, and Richard, 1993).

At steady state, activated carbon with a growing microbial colony can remove approximately 40% of the initial DOC from solution by one or more of three independent mechanisms: surface degradation, film degradation, and pore degradation (including in micropores) (Koch, Ostermann, Hoke, and Hempel, 1991). In a test of two carbon types at a Superfund site (wood treatment plant), both carbons had excellent total organic carbon (TOC) removal (minimum 80% removal after 64 bed volumes, influent 320 mg/L TOC). However, the same removal efficiency was not found for waters with an exceptionally high influent TOC concentration (50% removal after 64 bed volumes, influent 900 mg/L TOC) (Dahab, et al. 1991) A growing microbial community also is not easily removed during backwashing (Servais, Billen, Ventresque, and Bablon, 1991).

Pore diffusion appears to control the intraparticle mass transfer rate for DOC with either or both the pore and surface diffusion coefficients being linearly dependent on particle size and with the observed pore diffusion coefficient decreasing over time. Possible reasons for this decrease include the following: (a) the rapid initial diffusion is intraparticle, while the later, slower diffusion is micropore diffusion; (b) the diffusion path length increases as the pores fill; or (c) the displacement of previous adsorbed DOC by more strongly adsorbed DOC causes counter diffusion. Isotherm calculations for DOC sorption onto activated carbon showed that the percent adsorption after 15 days was nearly identical to that for 7 days. Also, it was determined that for a desired effluent concentration of 1 mg/L DOC ($c_e/c_i = 0.4$), the optimum empty bed contact time (EBCT) was between twenty and thirty minutes (Crittenden, et al. 1993).

Excellent removal of phenolic compounds from a groundwater spiked with 20 µg/L tricholorophenol (TCP) has been shown for activated carbon. The maximum adsorption capacity is dependent on the influent sorbate concentration, *i.e.*, capacity and rate of adsorption decrease with decreasing influent concentration (13 mg/L needed one hour contact while 4 mg/L needed a 24 hour contact time). The adsorption efficiency for a floc-blanket reactor was found to be equal to the adsorption efficiency for batch isotherm tests, indicating that a reactor or filter with sufficient contact time can achieve the maximum removal efficiency for the solute of interest. The adsorption rate of TCP onto activated carbon can be described by the homogeneous surface diffusion model (HSDM) in which an adsorbate molecule first diffuses through the carbon particle's stagnant liquid film layer before instantaneously adsorbing to the carbon's outer surface. The adsorbate then slowly diffuses along the carbon pores' inner surfaces (Najm, et al. 1993).

However, the capacity of granular activated carbon (GAC) for phenolic compounds in deionized water is decreased under anaerobic conditions. In the presence of oxygen, the TCP likely is converted to different, unmonitored compounds in the effluent. This results in an erroneously high estimation of adsorptive capacity (Adham, Snoeyink, Clark, and Bersillon, 1991). Phenol and *o*-cresol undergo oxygen-induced polymerization reactions on activated carbon that increase both the amount adsorbed and the strength of adsorption. The increases are dependent on the dissolved oxygen (DO) concentration. Seventy percent of the adsorbed phenol was recovered from Filtrasorb 400 activated carbon after adsorption under anoxic conditions while only 25% was recovered after adsorption under aerobic conditions, demonstrating that the adsorption under aerobic conditions led to stronger bonding between the phenol and the carbon. The molecular oxygen aids in the formation of acidic surface oxides on the carbon, which enhances dimer and trimer formation on the carbon surface. The polymerization also significantly increases the time required to reach equilibrium because it is the rate-limiting step. Adsorption is then limited by intracrystalline diffusivity rather than external mass transport resistance. For example, adsorption of phenol on Filtrasorb 400 activated carbon took 48 hours to reach equilibrium under anoxic conditions while it took 14 days to reach equilibrium under aerobic conditions. This increase in adsorption capacity in the presence of dissolved oxygen, however, does not hold for aliphatic organic compounds (Abuzald and Nakhla, 1994).

Chlorinated phenols are strongly adsorbed by activated carbon; however, biodegradation of these compounds can also occur on the carbon. Anaerobic degradation of the highly

chlorinated phenols, *i.e.*, tetra- and pentachlorophenol, will produce various lower chlorinated phenols, *i.e.*, tri-, di-, and monochlorophenols. This biodegradation and adsorption of the chlorinated phenols will occur simultaneously with pH significantly influencing the adsorption of compounds with acidic functional groups. Batch equilibrium adsorption data for eight chlorinated phenols on Calgon Filtrasorb 400 activated carbon in two concentration ranges at pH 7.0 and 30°C showed the adsorptive capacities increasing from pentachlorophenol to the trichlorophenols and holding fairly constant from the trichlorophenols to the monochlorophenols. The adsorptive capacity for the neutral molecules (monochlorophenols dominant) is higher than that for the ionized forms (pentachlorophenols dominant). The chlorine's position on the phenyl ring, however, has little influence on a chlorophenol's adsorption (Nelson and Yang, 1995).

The good fit of the Langmuir isotherm to the adsorption data suggests that a fixed number of accessible adsorption sites exists on the carbon for a given range of solute concentrations. A surface complexation model has been proposed in which the carbon's functional groups can be divided into two types: acidic (carboxyl, phenolic, quinonoid, and normal lactone) groups and basic (chromene and pyrone-like) groups. The surface complexation model fits the adsorption data for 2,4,5-trichlorophenol, 2,4-dichloro-phenol, and 4-chlorophenol for different pHs. Tests have shown only slight differences between isotherms for 2,4,5-TCP between pH 4.15 and pH 5.22, but significant differences between the isotherms at higher pH (> 6.5). Solution pH less than the pK_a (6.94 for TCP) does not significantly affect the adsorption capacity of the activated carbon, but when the pH is greater than

the pK_a, there is a linear decrease in adsorption capacity with the increase in pH (Nelson and Yang, 1995).

Benzene in groundwater also can be adsorbed on activated carbon. However, this adsorption may be retarded by one or more of the following reasons: fouling of the carbon by various components in groundwater; differences in adsorption and mass transfer kinetics of the various components; adsorption interference and competition by other compounds in groundwater, such as pesticides and herbicides; and interference by chemicals that precipitate on the carbon. At a benzene concentration of 20 mg/L, adsorption may be limited by film diffusion. However, at higher concentrations (50 mg/L), adsorption is not limited by film diffusion because of the larger concentration gradient available, and pore diffusion controls the rate of adsorption. Bacterial growth on the carbon surface may be either an advantage or a disadvantage. This strictly depends on the microbial population available (Rael, Shelton, and Dayaye, 1995).

It has been demonstrated at both a Superfund site and for an industrial wastewater that activated carbon will remove more than one organic compound from a solution. The Superfund site water contained various phenolic compounds (*i.e.*, pentachlorophenol, 4-methylphenol, and 2,4-dimethylphenol), pyrene, fluoroanthene, and unidentified total organic carbon (TOC), and color-producing compounds that were removed from solution by the carbon. However, competitive adsorption led to lesser adsorption efficiency as compared to the efficiency for pure test compounds (Dahab, et al. 1991). Competitive adsorption also reduced the capacity of carbon for the individual organics in the industrial wastewater, as compared to their respective single compound isotherms. Capacity reduction can be correlated with the percent of the total organic carbon (%TOC) in solution contributed by the target compound, *i.e.*, the smaller the %TOC, the larger the capacity reduction, because other compounds are available in sufficient concentration to compete for many of the adsorption sites. Mass transport limitation also can significantly reduce a compound's adsorption capacity, especially for large organic contaminants such as color agents (Ying, et al. 1990).

Activated carbon also can remove pesticides from solution. Atrazine and two of its degradation products, deethylatrazine and deisopropylatrazine, have been adsorbed from contaminated groundwater (200 µg/L atrazine filtered at 5 mL/min for 70 days through a 2 cm ID x 30 cm long filter column) (Selim and Wang, 1994). A sand filtration/carbon treatment system can remove a diversity of organophosphate, organochlorine, and pyrethroid pesticide residues down at least to their detection limit. The sand filtration step removes the pesticides associated with particulate matter while the carbon adsorbs the nonparticulate pesticides in the solution. Average removal efficiencies for the total treatment system were 79% for pyrethroids, 92% for organophosphates, and 96% for organochlorines (Moore, Hansen, Garnas, and Goodman, 1985). Activated carbon filters also can provide a good environment for microorganisms that may biodegrade certain organic molecules. The biodegradation often will increase the apparent adsorptive capacity of the carbon (Selim and Wang, 1994).

Inorganic (Non-Metal) Removal Capability

Activated carbon fiber has been shown to remove iodine and iodide compounds from acetic acid in water, methanol, and ethanol solutions. When compared to other conventional adsorbents (activated carbon, silica gel, alumina, NaY zeolite, Ag ion-exchanged NaY zeolite, and Ag ion-exchanged Amberlyst XN 1010), the activated carbon fiber had the greatest adsorptive capacity for the iodine and iodide compounds. Iodine removal was inversely related to iodine's solubility in the solution. The excellent removal by the fiber can

be explained by the unique structural characteristics of activated carbon fiber which promote fast adsorption. Since the fiber contains only micropores with a pore diameter less than 2 nm while activated carbon has a broader pore size distribution, the adsorptive capacity is greater for the fiber. This is because the major (stronger) adsorption sites are located only in the micropores with weaker adsorption in the meso- and macropores. Iodine diffusion to the strong binding sites is the rate-limiting step in the activated carbon adsorption, whereas this diffusion is eliminated in the fiber because the micropores are on the surface (Yang, Kim, Lee, and Kim, 1993).

Activated carbon also can reduce chlorite ions to chloride by having the oxychlorine species react with the radical sites, oxygen-containing functional groups, and metal ions on the activated carbon to form the radical entities ClO_2, Cl^o, and ClO^o. These then form Cl_2O_2, Cl_2O_3, HOCl, etc. with chloride, chlorate ions, and oxygen as final products. Increasing the initial chlorite concentration increases carbon's adsorption capacity for other compounds because the chlorate-forming secondary reactions are favored which increases the concentration of acidic surface functional groups and thus increasing the number and type of sites available for adsorption by not only chlorite but also other compounds. One gram of granular activated carbon removed 600 mg/L of chlorite from solution (Vel Leitner, De Laat, Dore, Suty, and Pouillot, 1994).

The presence of phenol or *p*-nitrophenol in solution or preadsorbed on carbon, however, will decrease its capacity to remove chlorite because many byproducts, such as chlorophenols, *p*-benzoquinone, dimerization, and carboxylation products, are formed on the carbon surface once the chlorite contacts the organics. These halogenation reactions occur in the granular activated carbon (GAC) bed both when the chlorite is in solution with the organics and when the chlorite-free organic solution is passed over chlorite-preoxidized activated carbon. Oxidation of activated carbon with chlorite apparently promotes the catalytic properties of the carbon surface. Other disinfectants such as NH_2Cl, Cl_2, ClO_2 also undergo halogenation reactions with organics in the presence of activated carbon. These byproducts may be less desirable than the organics originally in solution. Some of the byproducts formed from reactions of organics and disinfectants on the activated carbon surface include aromatic acids (benzoic acid, salicylic acid, hydroxynitrobenzoic acid, and nitrobenzoic acid), benzaldehyde, hydroxybenzaldehyde, 4-phenoxyphenol, 4-phenoxymethoxybenzene, 2,2'-dihydroxybiphenyl, benzofuran, 2,3-benzofurandione, chloronitrobenzenes, and nitrosophenol (Vel Leitner, et al. 1994).

Metal Removal Capability

Hexavalent chromium is effectively removed by a pH-dependent adsorption with the peak adsorption at pH 6 (Sharma and Forster, 1993). More than 80% of inorganic and organic mercury in a solution has been removed by a commercial granular activated carbon, with even greater removals resulting when humic acid or nitrilotriacetic acid (NTA) was added to the solution (initial solution, 10 µg/L Hg(II) and 5 mg/L of humic acid or NTA). Activated carbon from peanut shells is seven times more effective than commercially-available activated carbon at the removal and recovery of mercury from solution, possibly because the peanut hull carbon has a higher moisture content which may increase its porosity and make available more sorption sites. Peanut hull carbon also has a lower ash/higher carbon content (70 mg peanut hull carbon for adsorption of 20 µg/L in 100 mL solution versus 500 mg commercially available activated carbon for the same adsorption). Peanut hull carbon has lower decolorizing capacity and a moderate ion-exchange capability as compared to the commercially available carbon, implying that it will not be as suitable for organic adsorption. Peanut hull carbon adsorption also is not as pH dependent as commercially-available activated carbon. Rice-husk and coconut-shell activated carbon also has been effective in the removal of heavy metals from aqueous solutions. The adsorption process follows both the Freundlich and Langmuir isotherms with pore diffusion being only one of the rate-controlling steps (Namasivayam and Periasamy, 1993).

Microorganism Removal Capability

Historically, it has been believed that silver-impregnated activated carbon inactivated bacteria, *i.e.*, made drinking water 'safer,' possibly because low pH, lower temperatures, higher mineral matter, and phosphate concentrations could reduce bacterial action. Testing of a commercial silver-impregnated carbon filter showed that the concentration of *Salmonella typhi* was reduced more than 5 logs (99.999 percent) at a silver concentration of 50 µg/L and 1 hour of exposure; however, the concentration of *Pseudomonas aeruginosa* was reduced less than 50% at 50 µg/L silver and with 1 hour of exposure and the concentration of *poliovirus type 1* was not reduced at 50 µg/L silver and with 1 hour of exposure. Under most circumstances and with long-term use, the silver-impregnated activated carbon filters have negligible ability to remove microorganisms from solution (Bell, 1991). Silver has been fused into activated carbon and some ceramic filters in order to prevent biofilm growth in some household water filtration units, *i.e.*, Katadyn water filters.

Other Carbon-Based Filters

Carbonaceous residues such as wheat straw has been used to remove nitrogen from reclaimed wastewater in a nitrification/denitrification sequence. The wheat straw is then a

source of carbon for the microbial colonies that perform the nitrification and denitrification. The straw's capacity for nitrogen, ammonia, and nitrate, immobilization was found to be about 9 mg N/g. Significant reductions in BOD, organic carbon, chlorophyll, phosphorus, algae, and clay concentrations in the influent were also found (Lowengart, Diab, Kochba, and Avnimelech, 1993). The wheat straw substrate has a poor nutrient content which leads to the removal of nitrogen and phosphorus from the influent water by the microbial biomass (Diab, Kochba, and Avnimelech, 1993).

Ultrafiltration membrane pores (0.001 - 0.1 µm) are relatively large and can remove only those molecules and particles that are larger than the pores. Inorganic ions readily pass through these membranes. Activated carbon has been added to ultrafiltration systems in order both to remove the organics that cause early clogging of the filter and to sorb many compounds that would pass through the filter. The activated carbon concentration should be less than 600 mg/L for the best operational efficiency. Powdered activated carbon (PAC) is usually used in conjunction with ultrafiltration membranes because the smaller particle sizes of the PAC have considerably faster adsorption kinetics and reduce the required contact time. As with all activated carbons, the carbon concentration required to achieve a particular effluent concentration is directly related to initial concentration (Adham, et al. 1991).

Limitations of Activated Carbon

Activated carbon cannot desorb high boiling solvents and will polymerize or oxidize some solvents to toxic or insoluble compounds (Blocki, 1993). It has a very small net surface charge and is ineffective at removing free or hydrated metal ions, unless they are complexed with easily-adsorbed organics prior to filtration. However, once they are complexed with these insoluble organics, the complexed metals are readily adsorbed onto the carbon which results in the desired high removal rates (Anderson and Rubin, 1981).

CHAPTER 4 - LITERATURE REVIEW: PEAT MOSS

Peat is loosely defined as partially decomposed organic material, excluding coal, that is formed from dead plant remains in water in the absence of air. The physical structure and chemical composition of peat is determined by the types of plants (mosses, sedges and other wetland plants) from which it is formed. Peat is physically and chemically complex and is highly organic with its main components being humic and fulvic acids and cellulose .

Peatland development is controlled by several processes, including peat accumulation, *Sphagnum* acidification, and climate. The general movement from rich to poor fen and then to bog are primarily a result of peat accumulation. Peatland development can range from <1500 years to >2000 years and usually occurs in areas with gentle topography and where the prevailing climate has short, warm, moist summers and long, cold winters. Bogs and poor fens are *Sphagnum*-dominated while rich fens contain mostly brown mosses (Kuhry, Nicholson, Gignac, Vitt, and Bayley, 1993).

Peat accumulation causes the land surface to become separated from the mineral-rich ground water. Mesotrophic rich fens develop into oligotrophic poor fens that are further acidified by *Sphagnum*. Continued peat accumulation results in the development of ombrotrophic bogs, which depend exclusively on precipitation for nutrients and water. The rapid transition from rich fen (pH > 6) to poor fen and bog (pH < 5) is most probably a result of chemical factors, *i.e.*, the 5 - 6 pH transition range is also where the bicarbonate alkalinity becomes zero. Once this bicarbonate buffer is gone, the peatland is very sensitive to further oligotrophication and *Sphagnum* acidification (Kuhry, et al. 1993).

Peat Composition

Peat contains the products of inhibited plant and vegetable matter decomposition and may contain up to 15% bituminous substances, including a wide range of saponifiable (*e.g.*, C_{18}-C_{30} free fatty acids, fatty acid triglycerides, and non-glyceride esters) and unsaponifiable liquids (*e.g.*, long-chain hydrocarbons, alcohols, and steroids). At ambient temperature, the peat bitumen is a solid-liquid system. The solid phase consists of several different crystalline species of carboxylic acids and esters while the liquid phase is highly viscous and consists of a mixture of paraffins, carboxylic acids, alcohols, and esters. The flow behavior of the bitumen is similar to that of a yield pseudoplastic fluid. The behavior is extremely temperature sensitive because of both the melting or crystallizing of the crystalline minerals and the changing the polar interactions in the non-crystalline component. At ambient temperature using polarized light microscopy, the bitumen was found to contain many small crystallites (diameter, 5.4 µm). Using successive organic extraction steps, the peat bitumen was found to contain Wax (43.9%), Resin (37.9%), and Asphaltene (6.7%) with the remaining 11.5% containing some visible peat fibers but likely is mostly polymerized peat fatty acids and hydroxy acids. Infrared spectroscopy indicated that the polar species such as esters and acids are primarily in the Wax and Asphaltene fractions, while the Resins consist largely of non-polar constituents (Leahy and Birkinshaw, 1992).

Carboxylic acids and esters in the Wax fraction likely are the dominating rheological influence in the bitumen. They affect the peat's physical behavior because they crystallize at a low temperature and mechanically hinder flow, and because their secondary bonding increases the liquid's viscosity. The crystallizing species appear to be the esters of the fatty acids rather than the more polar acids and to be the species with molecular weights below 1200 (Leahy and Birkinshaw, 1992).

While the Wax consists primarily of medium and high molecular weight species, the liquid Resin is composed almost completely of low molecular weight material, such as paraffinic liquids, and carbonyl and hydroxyl species. No aromatic or unsaturated species appear to be in the Resin. The paraffinic liquids are non-crystalline with flow characteristics, at ambient temperature, of a low-viscosity Newtonian fluid. As the crystallinity of the Resin increases, the flow becomes yield pseudoplastic (Leahy and Birkinshaw, 1992).

The Asphaltene fraction appears to consist of similar-sized species to those in both the Wax and the Resin but is believed to contain more polar constituents. The crystallizing species in the Asphaltene are of relatively high molecular weight; however, analysis of the Asphaltene indicates that low molecular weight species are present and dilute the crystallizing species. The first fraction of the Asphaltene on an infrared spectra is a paraffin, followed by mixtures of saturated acids and esters, with esters. Acids increase in significance/concentration in the later fractions. The largest-sized fractions of the Asphaltene appear to contain several unsaturated compounds (Leahy and Birkinshaw, 1992).

Hydraulic Characteristics

Peat moss (*sphagnum* moss) is a fibric peat and is typically brown and/or yellow in color. It has easily identifiable undecomposed fibrous organic materials, and its bulk density is generally less than 0.1 g/cc. Because of its highly porous structure, peat moss can have a high hydraulic conductivity, up to 140 cm/hr. (Galli, 1990). Its chemical and physical structure (pore volume of 80-90% [Karamanev, Belanger, Chavarie, Chaouki, and Mayer, 1994]) encourages water retention, and it can contain up to approximately 90% water by weight (Leahy and Birkinshaw, 1992). Peat permeability varies greatly and is determined both by its degree of decomposition and the plants from which it came. Generally, the more decomposed the peat is, the lower its hydraulic conductivity. Peats are generally light-weight when dry and are highly adsorptive of water (Galli, 1990) because of their highly porous structure (Karamanev, et al. 1994). Peats lose most of their hydraulic conductivity when compressed.

Two different flow regimes exist in peat filters because of the peat's three-level, fractal-like structure, *i.e.*, the same shape of the structure is observed at three different magnifications. At low velocities, the liquid flows through the peat moss particles; however, at high velocities (above the critical velocity), the liquid mainly flows between the solid aggregates with only a small amount penetrating the particles forming the aggregates. When the liquid velocity exceeds 0.1 cm/s, flow resistance through the particles is too high, and the bulk of the liquid flows around the aggregates. The mass transfer mechanisms appear to be due to the following: 1) diffusional transfer at the smallest level; 2) convective or diffusional transfer (or both) at the second level, depending on the liquid velocity; and 3) convective transfer at the largest level (Karamanev, et al. 1994). A 50% change in a peat's moisture content can change its permeability up to five orders of magnitude (Mitchell and McDonald, 1992).

Peat moss' coarse structure likely causes the observed decrease in hydraulic conductivity as the water content is reduced. Peat also exhibits a hysteresis between the drying and wetting curves, likely because as the material dries out it becomes more hydrophobic and, consequently, more difficult to rewet (da Silva, Wallach, and Chen, 1993), with severely dried peats (>= 35% moisture loss) being exceptionally difficult to rewet. Possible reasons for this phenomenon include macropore collapse and high micropore suction-pressures. Drying also shrinks humic molecules, binding the color-producing, lower-molecular-weight fractions together. The peat initially will repel new water; however, continuing rewetting eventually will lead to water penetrating all pore spaces, saturating the peat, and flushing out any accumulated color-producing organic acids (Mitchell and McDonald, 1992).

Natural peaty clays have a high organic content (>20%) and are compressible because of void volume in the mix. However, the amendment of the peat with sand can greatly reduce its compressibility, which also will increase its bulk density and decrease its moisture content. When the sand to peat ratio is 1.76, the bulk density of the mixture increases from 1,310 kg/m^3 to 1,776 kg/m^3, and the moisture content decreases from >80% to 23% (Lo, Ooi, and Lee, 1990).

Organic Removal Capability

Peats can extract substantial amounts of either free-phase or dissolved hydrocarbons from water (between 50 and 90% of the starting wet volume and 63 and 97% of dissolved hydrocarbons from saturated solutions). In general, the best peats for hydrocarbon adsorption are low in fiber and birefringent organics and high in ash and guaiacyl lignin pyrolysis products. Because these parameters indicate the degree of peat decomposition, adsorption appears to increase as decomposition increases, possibly for the following reasons: (1) greater surface areas are associated with smaller particles; (2) chemical changes resulting from decomposition; or (3) inherent chemical or physical differences in the source plants. Sorption possibly results from the aromatic surfaces attracting the hydrocarbon while cross-linking side chains "trap it" and hold it in place. Another potential explanation of hydrocarbon sorption

to peat is that the intermolecular distances and area within the lignocellulosic polymer are suitable for absorption between basal lignin units. Inter- and intra-molecular forces between the lignin and the hydrocarbon control the competition between the two mechanisms (Cohen, Rollins, Zunic, and Durig, 1991).

Toluene is sorbed more slowly to peat than either benzene or *m*-xylene, yet toluene had much less variation in its sorption to different peat types than benzene and *m*-xylene. With sufficient contact time, toluene sorption capacity is similar to that of benzene and *m*-xylene. In free-phase experiments, the absorbencies exhibited by the specific peat types did not depend on the type of hydrocarbon sorbed, with the Maine *sphagnum* peat having somewhat less absorption per unit volume than other peats. This may be a result of the visibly larger pore size in *Sphagnum* peat compared to other peats. *Sphagnum* has more visible, preserved fibers, a higher water-holding capacity, and a relatively high porosity, which, along with pore size, type, and shape, may be significant factors in hydrocarbon adsorbency (Cohen, et al. 1991).

Peat moss can, however, shrink or swell in the presence of some organic compounds, possibly because sorption site availability increases in liquid sulfoxides, with the increase being dependent on humification despite the general decrease in oxygen/carbon ratio with humification. Swelling and/or shrinkage of the peat has been demonstrated by sorption of pure (>95%) methyl, tetramethylene, and propyl sulfoxides and propyl sulfones on dewaxed, acid-form peats. Apparently, the cellulose particles adhere to one another when dry. The addition of a liquid, even a nonswelling one, lubricates the particles so that initially they compact slightly (Lyon, 1995).

Alcohol sorption curves are similar, even with large differences in humification between the two peats studied, implying that the alcohol sorption sites within peats are not changed significantly by humification. Significant swelling was observed for peats immersed in propyl sulfoxide, demonstrating that the approximate limit of swelling, as found by Lyon and Rhodes, by solvents with molar volumes $\leq$ ca. 93 cm^3 mol^{-1}, can be exceeded when the liquid contains a strongly interacting functional group. The swelling limit for most alcohols is probably influenced more by the peat's basic sites rather than the acidic sites, and, therefore, different limits are possible for acidic and basic organic liquids (Lyon, 1995).

The binding of polycyclic aromatic hydrocarbons (PAHs) to both solid soil humic materials and dissolved humic substances appears to be controlled by both adsorption and partitioning with the filter media, with the partitioning term being the most important for largely nonpolar sorbates. The sorption of phenols and PAHs correlates well with their hydrophobicity. The sorption of nonpolar organics correlates well with the oxygen content of the organic matter in the peat, with the exception of a few polymers that have a high oxygen content. Nitro and hydroxyl groups on a sorbate molecule tend to strengthen the molecule's sorption because of the charge transfer interactions that occur between the sorbate and the peat. The correlation between a nonpolar organic's hydrophobicity and sorption capacity is not valid for aromatic amines where sorption exceeds the estimated bonding by five to ten times. The number of aromatic rings also appears to influence sorption capacity significantly. Fulvic acids are slightly more polar than humic acids, and, thus, they are slightly more water soluble and have slightly different sorption capabilities (Kopinke, Porschmann, and Stottmeister, 1995).

Peat can also leach organic compounds, especially colored organic matter such as humic and fulvic acids. The amount of leaching of colored compounds is dependent upon season (for an outdoor filter) and soil moisture. One possible explanation for the correlation of peat moisture and color distribution and intensity is the change in pH and water content during filtration. The peat showed a rapid initial rise in color and pH/acidity, followed by a gradual decline. The length of drying between filtration events indicates the size of the "store" of water-soluble, color-producing organic acids, especially in the top 3 cm where aerobic decomposition and oxidation also is occurring. When the filter is initially wetted, this "store" is released, and the effluent becomes colored as the decomposition products come into contact with water and become 'color' (Mitchell and McDonald 1992).

Inorganic (Non-Metal) Removal Capability

A peat-filter system has been developed for enhanced nitrogen removal or transformation in sanitary wastewater. The filter uses a layer of *sphagnum* peat moss placed below the weeping tile bed where nitrogen is assimilated into the fungal biomass, thus reducing the nitrogen content of the wastewater. Sixty to 100 percent removals have been achieved for nitrate levels up to 125 mg N/L (Robertson and Cherry, 1995). Peat is an excellent substrate for microbial growth, with large colonies of nitrifying and denitrifying bacteria typically present. It can assimilate nutrients and organic wastes because of its high C:N:P ratio, which often approaches 100:10:1. Long-term phosphorus retention in peat is related to its calcium, aluminum, iron, and ash content with the higher the content of each of the above constituents, the higher the retention capability (Galli, 1990). A peat filter system for treating septic tank effluent has been able to treat wastewater at a hydraulic loading rate of 40 L/m^2 of filter surface while maintaining a high effluent quality: NO_3-N (<5 mg/L), NH_3-N (0 - 17 mg/L), Organic-N (0 - 7 mg/L), BOD_5 (5 - 20 mg/L), DO (3 - 13.3 mg/L), TSS (5 - 15 mg/L), pH (5.3 - 6.5), and fecal coliforms (reduced by 99.99+ %). The major drawback to the system was the tea color of the effluent (Daigle, 1993).

Metal Removal Capability

Because of the lignins, cellulose, and humic and fulvic acids in peat, peat is highly colloidal, is polar, has a high cation-exchange capacity, and has a high specific adsorption capacity for transition metals and polar organics (Galli, 1990). *Sphagnum* moss contains an anionic polysaccharide ('sphagnan') that selectively binds calcium and other multivalent metal cations. As the dead moss slowly becomes peat, soluble sphagnan is gradually released. However, sphagnan is unstable, and in the mildly acidic conditions of peatland formation, it is slowly converted into humus or humic acid. Humic acid also binds multivalent metal cations, and its selectivity for Ca^{2+} is even higher than that of sphagnan, thus ensuring that peatlands are permanently decalcified (Painter, 1991).

Peat moss has been used to treat metal-bearing industrial effluents since it will adsorb, complex, or exchange various metal cations (Gosset, Trancart, and Thevenot, 1986). Peat has an excellent natural capacity for ion exchange with copper, zinc, lead, and mercury, especially at pH levels between 3.0 and 8.5. The peat contains polar functional groups such as alcohols, aldehydes, ketones, acids, and phenolic residues which chemically bind metal ions from a solution (Sharma and Forster, 1993). However, the sorption capacity of peat is finite and reversible and is controlled by the pH of the solution (Galli, 1990).

Immobilization of a metal by peat depends on (i) the metal ion capture chemistry, (ii) solute transport rates from the bulk solution to the adsorbent surface, and (iii) the transport rates and equilibria within the adsorbent's interstices. For metal adsorption on peat, film diffusion appears to be the rate-controlling step; although at small peat-to-metal ratios, internal mass transfer also greatly influences the sorption. A three-step model can be used to describe the metal immobilization process by peat: (i) solute mass transfer from the solution to the particle surface, (ii) ion-exchange reactions at fixed sites on the peat, and (iii) internal diffusion of solute. In general, the ion-exchange reaction is very fast compared to the other two steps and is not the kinetic rate-limiting step. At high peat concentrations, film and external mass transfers are most important while at low peat concentrations, intraparticle diffusion controls the reaction rate (Allen, Brown, McKay, and Flynn, 1992).

In buffered solutions, the order of sorption for four metal ions to peat is $Ni^{2+} > Cu^{2+} > Cd^{2+} = Zn^{2+}$, independent of peat origin. Above pH 3, copper binding is similar to nickel and is dependent upon the pH of the solution; cadmium and zinc present a similar pH dependence but are less strongly bound than the copper and nickel. Only the nickel cation, however, is bound strongly enough not to be desorbed when the pH is dropped to below 1.5 (Sharma and Forster, 1993).

In unbuffered solutions, the pH drops between 0.2 and 0.6 pH units during filtration for all metal-peat combinations tested (Gosset, et al. 1986) because of the release of humic and fulvic acids during adsorption or ion exchange (Sharma and Foster, 1993). Unsieved and non-acidified oligotrophic or eutrophic peat samples seem to bind copper more rapidly and efficiently than sieved and acidified ones, possibly because the structure of the peat is changed during acid pretreatment. The sorption curves for the metals are not linear, regardless of the peat-metal combination, indicating that the peat-metal complex stoichiometry and thermodynamics are probably dependent both on the free metal concentration and on pH, which varies in unbuffered solutions.

Although saturation limits of 200 mmol metal/kg dry weight peat were observed in buffered solution, sorption saturation (even at 0.1 M metal in 50 g/L peat) was not observed in unbuffered solutions. Maximum removal could be achieved when the metal concentration in the buffered soluton was in the 0.1 - 1 mM range, provided that there is adequate contact time (Gosset, *et al.* 1986). *Sphagnum* moss has been shown to remove iron (75% reduction) and manganese (25%) from acid mine drainage in Pennsylvania ("Moss Tested to Remove Manganese from Mine Drainage," 1984).

Sphagnum moss peat concentrations ranging from 4 to 40 g/L can effectively remove hexavalent chromium from solution (10 to 1000 mg/L Cr(VI)), especially when the ion concentrations are low. At equilibrium pH of 2.0, almost complete removal of Cr(VI) can be achieved when chromium concentrations are less than 100 mg/L, while at equilibrium pH of 1.5, 64% Cr(VI) removal can be achieved when chromium concentrations are less than 1000 mg/L. The sorption is pH dependent, with the optimum range being 1.5-3, and is controlled by (i) chemical reduction, *i.e.*, Cr(VI) to Cr(III); and (ii) adsorption of the mainly Cr(VI) species. The chromium is strongly bound, and little desorption occurs in low molarity caustic solutions. In high molarity caustic solutions, the peat itself 'disintegrates' (Sharma and Forster, 1993).

Limitations of Peat Filters

The release of color upon wetting is one problem with peat. Another potential problem is that peat may leach some nutrients, depending on the soil and water chemistry and water level. *Sphagnum* peat generally will release significantly more phosphorus and ammonium than *Carex* peat with the water quality determining the extent of nutrient release, especially in waters with a high sulfate concentration. Temperature also influences the amount of ammonium, potassium, and phosphate leached. Nutrient leaching will increase two to

three fold after the peat has been frozen (Koerlsman, Van Kerkhoven, and Verhoeven, 1993).

Stormwater Runoff Treatment

Urban road runoff generally has large concentrations of heavy metals and particulate organic carbon, as well as high alkalinity. Peat moss has been used as a growth medium for plants, such as red maple and cranberry seedlings, to treat urban stormwater runoff containing lead and zinc. In general, metals in acidic swampwater were more available to the plants than those in alkaline runoff and uptake of the metals usually increased with decreasing pH and decreased with increasing soil organic matter content. However, soluble organic acids can mobilize heavy metals into solution, even those in alkaline runoff water (Vedagiri and Ehrenfeld 1991).

Peat-sand filters (PSF) have been proposed to treat urban runoff. The PSF is an aerobic, "man-made" filtration system, unlike older sand or peat filtration systems that use naturally occurring soils as the filter. The peat-sand mixture layer must be manufactured as it does not occur in nature. A PSF can be expected to remove most of the phosphorus, BOD, and pathogens, and with a good grass cover, other nutrients (Galli, 1990).

The Peat-Sand Filter System designed by the Metropolitan Washington Council Of Governments (Washington, D.C.) would have a good grass cover on top underlain by 12 to 18 inches of peat. The peat layer is supported by a 4-inch mixture of sand and peat which is supported by a 20- to 24-inch layer of fine to medium grain sand. Under the sand is gravel and the drainage pipe. The mixture layer is needed because it will provide the necessary continuous contact between the peat and the sand layers and ensure uniform water flow. Because the PSF is a biological filtration system, it will work best during the growing season when the grass cover can provide the additional nutrient removal that will not occur in the rest of the filter (Galli, 1990). The expected pollutant removal efficiencies are given in Table 12.

Table 12. Peat-Sand Filter Pollutant Removal Efficiencies (Source: Galli, 1990)

Pollutant	Removal Efficiency (%)
Suspended Solids	90
Total Phosphorus	70
Total Nitrogen	50
BOD	90
Trace Metals	80
Bacteria	90

CHAPTER 5 - LITERATURE REVIEW: COMPOST

Composts made from yard waste, primarily leaves, have been found to have a very high capacity for adsorbing heavy metals, oils, greases, nutrients, and organic toxins due to the humic content of the compost. These humic compounds are stable, insoluble, and have a high molecular weight. They act like polyelectrolytes and remove the toxicants from the runoff either by adsorption or ion-exchange. The exact content of and aging process for the composts used by W&H Pacific/CSF Systems, Inc. are not public knowledge with the result that the filter installation-and-maintenance company supplies the compost to the stormwater treatment device owner.

The composted leaf filter was developed by W&H Pacific for Washington County (WA), the Unified Sewer Agency, and the Metropolitan Service District of Washington County (W&H Pacific, 1992a). The filter consists of a bottom impermeable membrane with a drainage layer above it. Above the drainage layer is a geotextile fabric upon which rests the compost material. The actual toxicant removal occurs in the compost layer by filtration, adsorption, ion exchange, or biodegradation, or by a combination of these processes.

The composted leaf filter is advertised as an improvement over other stormwater treatment devices, such as detention ponds and grass swales, because the square footage required for the filter is much smaller than for the other devices. A small presettling area (less than one minute detention time) is recommended; otherwise, the larger particles and floatables will prematurely clog the filter and reduce its treatment efficiency. Filter design was based on permeability tests performed by W&H Pacific and the design flow was selected as 2.25 gallons per minute (0.30 m^3/min), which gives a required compost bed surface area of 200 ft^2/cfs (60,435 m^2/m^3/sec.).

The results from the testing of a prototype Compost Storm Water Filter System (CSF) are given in Table 13. This filter was located where the drainage area is 74 acres (3.9

acres highway, 70 acres mixed residential).

A three-year testing program on the CSF has shown that the filter is excellent at removing metals and hydrocarbons from the runoff. Sediment accumulation, always a potential problem for any filtering system, was, during the 1992-93 testing season, approximately 74 ft^3 (2.1 m^3) with an average thickness range of 0.25 to 1.27 ft (0.07 to 0.4 m). During the 1993-94 season, 111 ft^3 (3.1 m^3) of sediment with an average thickness of 0.5 to 1.2 ft (0.14 to 0.4 m) collected in the system (CSF Systems, 1994).

Based upon the sample results at the location of the compost filter, the first flush of a storm had the heaviest pollutant loadings, and the filter had the highest removal efficiencies during this first flush. This indicates that the CSF System is capable of treating a shock loading of pollutants while producing an acceptable effluent. The average first flush removal rates for the three years of operation are given below in Table 14.

CSF Systems, Inc., the manufacturer and distributor of the compost filter, outlines the advantages and disadvantages of this compost system. One advantage is that the filter has a very high buffering capacity in the alkaline range. When the influent is between pH 6.7 and 8.3, the effluent is consistently between pH 7.0 and 8.0. However, because the media is an ion-exchange resin, whenever a pollutant sorbs to the media, an ion is 'leached off.' In the case of the compost, soluble phosphorus is one of the ions that is leached off during ion exchange (influent, 0.09 - 1.0 mg/L; effluent, 0.29 mg/L). Soluble phosphorus likely is released from the captured solids through microbial action and since the compost only has a weak anion exchange capacity, most of the soluble phosphorus is not removed from the water once it is leached from the compost. Testing has also shown an increase in boron and nitrate in the effluent of the compost filter (CSF Systems, 1994).

Table 13. Compost Filter Pollutant Removal Efficiencies (Source: CSF Systems, 1994)

Pollutant	Influent/Effluent Concentration Range	Removal Rate (%)
Turbidity		82
Total Solids		49
Suspended Solids		92
Total Volatile Suspended Solids	0-90 mg/L Influent; 0-14 mg/L Effluent	89
COD		70
Settleable Solids	0-4 mL/L Influent; 0.05-0.1 mL/L Effluent	95
Total Phosphorus		49
Ammonia		60
Total Kjeldahl Nitrogen		57
Copper		7
Zinc		83
Lead		83
Aluminum		84
Iron		91
Petroleum Hydrocarbons		84
Oil and Grease		81

Table 14. Compost Filter Removal Efficiencies – First Flush

(Source: W&H Pacific, 1992b; CSF Systems, 1994)

Pollutant	Removal Rate (%)
Turbidity	86
Total Solids	63
Total Suspended Solids	94
Settleable Solids	98

Total Volatile Suspended Solids	97[*]
COD	79
Total Phosphorus	63
Ammonia	65
Total Kjeldahl Nitrogen	72
Copper	83
Zinc	86
Lead	86
Aluminum	88
Iron	93

* Results are from the first year of operation only.

CHAPTER 6 - LITERATURE REVIEW: ZEOLITE

Adsorbents must be sufficiently selective and have adequate capacity and stability to achieve the required separation economically over a prolonged period of time. To get the required capacity, the adsorbent must have a high specific surface area, *i.e.*, be highly porous with fine pores (micropores). Furthermore, most important adsorbents use physical adsorption (multilayer) rather than chemisorption in which the capacity is limited to monolayer coverage (Ruthven, 1988). Zeolites are preferred as adsorbents in the chemical process industry because they are inorganic, non-flammable, and can withstand very high temperatures (Vaughn, 1988). Generally, they are porous aluminasilicates which may occur naturally but also can be synthesized (Blocki, 1993). They have been used in such diverse applications as natural gas purification (chabazite), radioactive waste disposal (clinoptilolite), ammonia recovery from sewage effluents (clinoptilolite), and various petroleum and petrochemical catalyst applications (erionite, mordenite) (Vaughn, 1988).

Physical Characteristics

Zeolites occur naturally in basaltic lava, in specific rocks subjected to moderate geologic temperature and pressure, and in altered and reacted volcanic ash deposits (Vaughn, 1988). Clinoptilolite is the most abundant naturally occurring zeolite. The formula of one cell of clinoptilolite is $(Ca,Na_2,K_2)_3[Al_6Si_{30}O_{72}] \cdot 24H_2O$. It has a two-dimensional 8-ring and 10-ring channel structure with the largest cavity measuring 4.4 x 7.2 Å. Zeolite surface chemistry is similar to that of smectite clays with the difference between the two being that natural zeolites may be millimeter or greater sized particles and do not exhibit shrink-swell behavior (Haggerty and Bowman, 1994).

The primary building block of zeolite is a tetrahedron of four oxygen atoms surrounding a central silicon atom $(SiO_4)^{4-}$. Zeolite polyhedra are connected by shared oxygen atoms on the corners, and these polyhedra connect to form the various specific zeolite crystal structures. Different combinations or arrangements of the same polyhedra may give numerous distinctive zeolites. Other elements, such as Al, Ga, Ge and Fe (Haggerty and Bowman, 1994), may be substituted for the silicon, provided that they "fit" into the center of the four tetrahedral oxygen atoms without too much strain on the oxygen bonds and that the resultant structure is electrically neutral (Vaughn, 1988). Union Carbide scientists in alumino-phosphate chemistry recently have expanded zeolite compositions to include about 13 elements, including Li, Be, B, Mg, Co, Mn, Zn, P, As, and Ti (Haggerty and Bowman, 1994). These variations in the chemistry in the basic structure change the pore sizes available for sorption and therefore alter the selectivity that can be achieved by a zeolite (Blocki, 1993).

Zeolites often are called molecular sieves because their crystalline framework has channels (pores) and interconnecting voids of molecular size (3 to 10 Å) (Vaughn, 1988). Zeolite species are often specified by letters after their name. Zeolite A has 8-member oxygen rings with a void size of 4.3 Å in the Ca^{2+} form, 3.8 Å in the Na^+ form and 3.0 Å in the K^+ form. X and Y zeolite pores, both of which have 12-member oxygen rings and whose frameworks are identical, are larger, having a free aperture of about 8.1 Å. The difference between the X and Y zeolite is the Si/Al ratio which controls the cation density and therefore affects its adsorptive properties. The zeolite with the intermediate pore size has a 10-member oxygen ring and has a pore size of about 6.0 Å (Ruthven, 1988). The ability to control access to the reactive sites by selecting the zeolite with the pore size in the desired range, as well as the

size and stereochemistry of the site itself, makes molecular-level control of chemical reactions possible (Vaughn, 1988).

Zeolite Synthesis

Zeolite synthesis is usually a batch process run at one of the following conditions: (1) 90-100°C, 1 atm. pressure, pH > 10; (2) 140-180°C, 5 - 10 atm., pH > 10; or (3) 100-180°C, water + "amine" autogenous pressure, pH > 10. The metal phosphates, a relatively new class of zeolites, are made under conditions similar to (3) above, except that the pH is between 3 and 6 (Vaughn, 1988). By varying the chemistry in the basic structure, different pore sizes and different selectivities can be achieved (Blocki, 1993).

Once the crystal synthesis is complete, the zeolite is mixed with a binder, and then formed into beads, pills, tablets, or extrudates. In most applications, the binder must be completely inert to avoid side reactions. Fabrication of the zeolite pellet is difficult because one must avoid plugging the pores with the binder and must avoid crushing the crystalline structure in high-pressure pilling processes. Most applications require maximum activity or sorption capacity, and, therefore, the manufacturing process tries to maximize zeolite content and minimize binder content (Vaughn, 1988).

Zeolite Adsorption/Ion-Exchange Characteristics

Because micropore size is uniform in zeolites, these adsorbents have a rather sharp cut-off of sorption with increasing molecular size. Although the framework primarily determines the pore size, the free aperture, particularly in the smaller 8-ring sieves, may be modified by ion exchange, again tailoring the zeolite to a specific effective pore size. Zeolite also is a polar molecule, and it has some unique affinities which are promoted by the ability to fit a particular molecular shape into a pore. These features also contribute to the ability of zeolite to be a highly selective adsorbent. Adsorption forces for zeolites can be divided into van der Waals forces, induced dipole interactions, and other electrostatic forces (polarization, dipole and quadrupole interactions). Van der Waals forces affect any sorbate-sorbent pair because they depend on the surface (micropore) geometry and increase with the polarizability of the sorbate molecule. Molecules which just 'fit' in the pore channel have maximum van der Waals interaction energy. By contrast, electrostatic forces, except for polarization energy, require both a surface electric field, *i.e.*, polar or heterogeneous adsorbent, and a dipolar or quadrupolar sorbate molecule (Ruthven, 1988).

When Al^{3+} is substituted for Si^{4+} in the zeolite framework, a net negative charge on the molecule results. This is compensated for by a 'nonframework' cation (*e.g.*, Na^+), which is 'held' in the pores of the structure. Because this cation is not a part of the crystalline lattice, it is relatively mobile and easily exchangeable for other cations (Vaughn, 1988). Ion-exchange and adsorption processes for zeolites often are even more complicated than for organic ion-exchange resins because the zeolite has two distinct pore structures: micropores in the crystals and macropores in the binder, both of which can participate in sorption (Robinson, Arnold, and Byers, 1994). Zeolites have internal and external surface areas of up to several hundred meters squared per gram. They can have cation-exchange capacities (CECs) of up to several equivalents per kilogram (Haggerty and Bowman, 1994).

Because of the exchangeable cations, zeolites are polar adsorbents. Molecules such as water or ammonia (high dipole), CO_2, N_2 (quadrupolar) or aromatic hydrocarbons (π layer interaction) therefore adsorb more strongly than nonpolar compounds of similar molecular weight. This affinity generally increases with increasing charge on the exchangeable cation and decreasing cation radius, but its effect may be masked by water, which, because it is strongly bound to a zeolite, will reduce the zeolite's affinity for other, less polar molecules. Aqueous sorption has considerable amounts of water present in the intracrystalline fluid (Ruthven, 1988).

Although most zeolites are strongly hydrophilic (because the strongly polar water molecule interacts with the cation), the zeolites with a high silica content (nonpolar surfaces) are actually hydrophobic because water is adsorbed less strongly than most organics. The adsorption is limited to van der Waals forces, and water is adsorbed less strongly than the more polarizable organics (Ruthven, 1988). The hydrophilic zeolites may not separate volatile organic compounds (VOCs) well in a humid atmosphere (Blocki, 1993).

Liquid and concentration-dependent surface diffusion both contribute to macropore diffusion (Robinson, et al. 1994). Diffusivities (at 600 K) range from 10^{-6} - 10^{-7} cm^2/s for benzene and p-xylene to 10^{-14} - 10^{-15} cm^2/s for hexamethylbenzene and anthracene. Although diffusivity changes cannot be correlated directly to molecular weight, molecular length, or critical molecular diameter sequence, the diffusivities generally tend to decrease with increasing sorbate size. Diffusivity instead correlates well with the sorbate's moment of inertia, suggesting that restrictions of the rotational freedom of the sorbate molecule affects diffusivity. This pattern indicates that the diffusion of sterically hindered planar molecules within the pores of a zeolite is controlled primarily by entropy effects, not because the pore size is too small. Therefore, a sharp cutoff of sorbate size exists and, for molecules larger than the cutoff and whose deformation is sterically hindered, essentially no intracrystalline pore penetration and sorption exist (Ruthven and Kaul, 1993b).

Organic Removal Capability

Hydrophobic zeolites generally are non-flammable, temperature-resistant (up to $1000^{\circ}C$), inert to many polar and nonpolar solvents, and efficient adsorbents for a wide concentration range (Blocki, 1993). The saturation capacity is expected to be one molecule per pore, and the adsorption isotherms for many higher weight aromatic hydrocarbons, such as benzene, toluene, xylene, mesitylene, tetramethylbenzene, naphthalene, hexamethylbenzene, dimethylnaphthalene, and anthracene, approach this saturation capacity. There is very little difference between either the isotherms or heats of sorption for different aromatic sorbates with the same carbon number. Therefore, for sufficiently large molecules, steric restrictions of the pores reduce the contact between neighboring molecules and, therefore, their potential for interaction which would prevent sorption (Ruthven and Kaul, 1993a).

The higher molecular weight aromatics are very strongly adsorbed, and intracrystalline diffusion is quite slow and temperature dependent. The sorption capacity, however, is essentially independent of temperature, reflecting the tendency of the larger molecules to average out the effect of adsorbent heterogeneities (Ruthven and Kaul, 1993a). Zeolites can also sorb unsaturated hydrocarbons with the sorption 'strength' pattern as follows: aromatics > olefins > paraffins (Ruthven, 1988). However, unlike activated carbon with its variety of pore sizes, hydrophobic zeolite is slower at separating some relatively common solvents such as xylene because the solvent molecules' diameters are less than the hydrophobic zeolite's pore sizes (Blocki, 1993).

Modifying the surface of a zeolite by initially performing ion-exchange with a cationic surfactant can increase the sorption capacity for organics that do not sorb well to natural zeolite. Quarternary amine (HDTMA)-modified zeolites can remove chlorinated aliphatic compounds and benzene derivatives from aqueous solution by a partitioning-like mechanism without lowering the zeolite's naturally high-sorption affinity for transition metal cations such as lead (Eyde, 1993; Haggerty and Bowman, 1994).

Inorganic Removal Capability

Because of its net negative charge, natural zeolite does not sorb anions well, if at all (Eyde 1993). Surface modification, such as ion-exchange with cationic surfactants, has improved the ability of zeolite to sorb anions and other compounds that natural zeolite did not sorb well. These sorbed cationic surfactants alter the surface charge of the zeolite, thus allowing it to sorb anions and other compounds of interest. Removal of inorganic oxyanions, such as chromate, selenate and sulfate from aqueous solutions improved from nearly zero sorption when a clinoptilolite-dominated zeolite was modified by 140 mmol/kg zeolite (15 meq/g) of hexadecyltrimethylammonium (HDTMA). Anion sorption was greatest when the HDTMA satisfied the zeolite's total external cation-exchange capacity. Anion retention (4 mmol/kg for CrO_4 and >2 mmol/kg for SeO_4 compared to 1 mmol/kg for both on natural,

unmodified zeolite) resulted from the formation of an HDTMA-anion precipitate on the zeolite surface (Eyde, 1993; Haggerty and Bowman, 1994).

Some zeolites are unstable at low pH because the aluminum in the framework is hydrolyzed, and so one approach to exchanging transition metals at low pH is to first form ammonia complexes by dissolving them in dilute aqueous ammonium hydroxide and then carrying out the exchange at high pH (Vaughn, 1988). The HDTMA-modified surface, however, is stable at low pH, higher ionic strength and with organic solvents (Eyde, 1993; Haggerty and Bowman, 1994). For the US Bureau of Mines, zeolites are an alternative to conventional precipitation removal techniques for metals such as lead (Eyde, 1993).

CHAPTER 7 - LITERATURE REVIEW: FOREST PRODUCTS AGRO-FIBER

Forest Products Agro-Fiber

The Forest Products Research Lab agro-fiber product was developed as both an economic oil adsorbent and as an economic ion-exchange media for pollutant removal from water. Kenaf and jute fibers, along with forest wastes such as barks and pine needles, have been found to efficiently remove copper from water. Chemical treatment of the kenaf with reactive yellow-2 significantly increased the capacity of the kenaf for copper (Forest Products Research Lab, 1995).

CHAPTER 8: MASTER'S THESIS PROJECT REVIEW

Project Background and Objective

The initial scope of this project was to determine the design variables for the sand filter (depth, grain size) that would polish the effluent from the settling chamber of the Multi-

Chamber Treatment Train (MCTT), a stormwater runoff treatment device that has been designed by Dr. Robert Pitt at the University of Alabama at Birmingham to treat the runoff from small, problem source areas, such as service stations and maintenance yards. The MCTT consists of three chambers, the sump (grit removal), the settling chamber, and the filter. This device is designed to be installed at the storm sewer inlet from a problem source area with the effluent from the device being directly discharged to the storm drain system. The appeal of this device to owners of small, problem source areas is that the device is low maintenance (1 - 2 times per year maximum) and low cost for construction and operation.

A filtration column was constructed using the design guidelines from Austin (18" [46 cm] of sand on top of a gravel underlayer) in 1000 mL graduated Kimax burets (acquired from Fisher Scientific). The first tests evaluated the water retention in the column, steady state flow rate through the media and the quantity of solids that can be loaded on the column before 'clogging.' Mass balance analyses were then performed by filtering a sodium chloride solution (4 g/L) through the column followed by filtering repeated slugs of 18 MΩ water. These tests with NaCl determined the water retention and exchange of the material with repeated flushings. Stormwater runoff was then filtered, and grab samples were collected and analyzed for toxicity (Microtox™), turbidity, and conductivity. The results of all these tests indicated that the filter was not performing as expected based on the Austin results. Permanent retention of toxicants was not occurring in the column; instead, trapped toxicants were displaced from (flushed out of) the pores during subsequent tests or rinsings. Because of these results, this master's project was expanded to evaluate several prospective stormwater filtration media using the filter construction specifications from Austin. Since the physical straining in the sand filter was not effective at permanently retaining the toxicants, other media were selected based on their ability to remove pollutants of interest through chemical reactions, either adsorption or ion exchange. The filtration media used in the continuation of this research included the following: activated carbon, peat moss, zeolite, compost, Enretech (a cellulose waste), and a chemically-modified agro-fiber. Sand was also used as a comparison, since it is the industry standard. These materials had a wide range of expected performances and included relatively expensive media known to provide excellent treatment (activated carbon) and waste materials (composted leaves, Enretech, and the agro-fiber) with uncertain removal characteristics. Although their expected pollutant removal efficiencies were low (Agnew, 1995), two filter fabrics were also selected for testing. One of the fabrics (EMCON fabric from BAMCON) was available commercially for stormwater treatment at the time of acquisition, and the other (Gunderboom) was being used in the MCTT at the Transportation Parking Lot at UAB to distribute water equally across the surface area of the filter. Past testing of the Gunderboom fabric found that water will not flow through the fabric until a two-to-three inch (5 to 7.5 cm) head had built up on it. Therefore, the Gunderboom can be used on top of a conventional filter to evenly distribute water across the filter surface and prevent bypassing of part of the filter (Pitt and Clark, 1996). A secondary purpose was to determine and describe potential drawbacks to the use of each of the media. A new testing program was designed, and included the following components:

• sediment loading on media before clogging

• effects of pH and ionic strength on adsorption of pollutants

• long-term tests to measure chemical breakthrough

It was decided that six grab samples should be collected during the bench-scale pH/ionic strength tests because statistical significance for most parameters could be determined using the Wilcoxon signed-rank method to less than 0.01, yet the required number of laboratory analyses could be held to a reasonable level. It was also decided that an a minimum of five samples would be collected during the long-term tests.

The media described below were the media of interest for this research. These media were selected because of their prior use in either stormwater or wastewater treatment devices, or both. A comparison of the pollutant removal pathways for different media is in Table 15. The only difference between sand filters and other media is the ability of the organic media to act as an ion-exchange resin. Both sand and organic filters currently in use have a pretreatment area that is a sedimentation chamber and that slows the runoff velocity. Both media strain out particles to the size limit imposed by the pores of the media. Sand can adsorb pollutants once the filter is aged, *i.e.*, when a microbial biofilm has formed on the surface. In order to determine the appropriate filter media, the properties of the individual media must be compared, as they are in Table 16.

Table 15. Filtration Media Pollutant Removal Pathways

(Source: Claytor and Schueler, 1996)

Removal Pathway	Sand Filters	Organic Filters
Sedimentation	In pretreatment cell	In pretreatment cell
Straining	In media	In media
Adsorption	By organics on filter surface	Peat or compost media
Microbial Action	On filter surface	On filter surface

Plant Uptake	None, unless cover crop	None, unless cover crop
Infiltration	None, unless open system	None, unless open system
Dissolved Solids Leaching?	Yes	Yes
Nitrification/ Denitrification	Nit.: Yes Denit.: No	Nit.: Yes Denit.: No

Table 16. Physical/Chemical Properties of Filter Media
(Source: Claytor and Schueler, 1996)

Property	Sand	Compost	Peat
Hydraulic Conduct. (cm/hr)	3.3	unknown	0.025-140
Water Holding Capacity (cm/cm)	0.14	unknown	0.01-0.2
Bulk Density (gms/cm)	2.65	1-2	<0.1-0.3
pH	N/A	7.8	3.6-6.0
Organic Matter (%)	<1	30-70	80-98
Cation-Exchange Capacity	1-3	66	183-265
Total P (%)	0.0	<0.1	<0.1
Total N (%)	0.0	<1.0	<2.5
Filtration Efficiency after 0.45 m (%)	93	16	47

Experimental Procedure

Filtration Column Construction.   Because these experiments involved testing of the filtering media as they are used in the field, the columns were constructed according to the design guidelines provided by the City of Austin (1988) and rinsed according to the rinsing directions supplied by CSF Systems, Inc. (1994). The filtration columns used in these experiments were Kimax-brand, one-liter, graduated burets (from Fisher Scientific) (inner diameter = 48 mm) or, for the filter fabrics, borosilicate glass (from Curtin Mathison Scientific) (inner diameter = 45 mm) cut to approximately the same length as the burets. The ratio of column diameter to median filter grain particle size for the sand filter (the media used to determine filter height and column diameter) was greater than 100. According to other researchers, this should be sufficient to avoid significant wall effects and to get the Reynolds number for flow through the filter to be greater than 20 (Clark, et al., 1992).

The filtration media columns were constructed first by cutting a piece of fiberglass window screen, purchased at a local hardware store, into a 10 cm x 10 cm square. This screen was placed in the bottom of the buret and approximately five centimeters of epoxy-coated fish-tank gravel (from Wal-Mart) was poured on top of it to the 1000 mL mark. The column was then rinsed with one hundred milliliters of tap water. Fifteen centimeters of sand was then added on top of the gravel. The sand was then rinsed at least twice, in one hundred milliliter increments, with tap water. After the sand layer had drained, approximately thirty centimeters of the media of interest was added to the column on top of the sand underlayer. After the media of interest had been added, the filters were then rinsed several times with tap water in accordance with the directions supplied by CSF Systems, Inc. for constructing the compost filter and then allowed to stand overnight before use as per their specifications. Filter fabric test columns were constructed by attaching a 15 cm x 15 cm piece of the fabric to the bottom of the glass tubes with stainless steel hose clamps which were purchased locally. The fabric and column were then set in a borosilicate glass funnel (from Fisher Scientific). All columns were then placed on a carousel that had been constructed for these tests.

Effluent samples were collected in the appropriate bottles. The need for homogeneity of the influent dictated the need for a flow splitter. The flow splitter was designed to allow a single influent flow to be randomly split into a maximum of ten equal effluent flows. Delrin plastic was used to construct the splitter, with the machining on the flow splitter done by MGM Machining in Helena, AL. A plexiglass support was constructed for the flow splitter so that the splitter was high enough to allow the runoff to flow down the tubes at a 45-degree angle from the base of the splitter. This 45-degree angle was assumed to be sufficient to prevent particle deposition on the insides of the tubes, even during low flow conditions. In order to address the concern about leaching from the construction materials, all construction materials were leach-tested by soaking them in approximately 400 mL of 18 MΩ water for about 65 hours. The water was then tested for toxicity, turbidity, pH, conductivity, color, organics, pesticides, and heavy metals. Results of these tests showed that the use of the Delrin Plastic, Plexiglas, Black Plastic Fittings, and Reinforced PVC Tubing on the sections of the apparatus that came into contact with the stormwater runoff would be acceptable. The fiberglass

window screen was found to be toxic to the Microtox™ luminescent bacteria when the screen was left to soak overnight. However, occasional rinsing of the screen did not add toxicity to the water.

The filtration media used in this project included the following:

- sand (uniformity coefficient of 1.45, d_{10} = 0.31 mm, d_{60} = 0.45 mm, Porter Warner Industries, Birmingham, AL);

- activated carbon (Aquatic Eco-Systems, Apopka, FL);
- peat moss (*sphagnum* moss, K-mart, Inverness, AL);
- zeolite (Aquatic Eco-Systems, Apopka, FL);
- compost (specific municipal leaf compost, Stormwater Management, Inc., Portland, OR);
- ENRETECH I (cellulose waste fiber used as oil sorbent, RAM Services, Birmingham, AL);
- Forest Product agro-fiber (chemically modifed kenaf fiber, Forest Products Research Lab);
- Gunderboom filter fabric (used in oil spill cleanup by Amoco, Polar Express, Alaska); and
- EMCON filter fabric (originally marketed in stormwater inlet device, Foss Environmental Services, Seattle, WA)

Because of the variability in the hydraulic conductivities and contact times of the adsorbent media alone, sand was mixed with all media (approximately half and half by volume), except the fabrics, before the mixed media was added to the filtration columns. In order to get a better "distribution" or "mixing" of media for the Enretech and Forest Products material, these materials were broken apart by hand (unclumped for the Enretech and torn apart for the Forest Products material) into small pieces. According to Stormwater Management, Inc. (formerly CSF Systems), the compost was generated from only certain types of leaves in order to achieve the maximum adsorption capacity and, therefore, maximum pollutant removal from the stormwater of Portland, OR (John Knudsen, personal communication, 1994). However, visual inspection of the compost received from them revealed pieces of glass, indicating that the selection process for the compost generated in mass quantities is not as particular as it was for the prototype devices. Because this compost is different than that used in the prototype, pollutant removal efficiencies likely are different than that described in the literature review. When selecting the compost to be used in the filter, no large pieces of twigs or glass were chosen.

Collection of Stormwater Runoff.   For all the filtration tests, stormwater runoff had to be collected. For the preliminary investigations on the sand filter, the runoff used was a composite of runoff received from Stafford Township, NJ. The unpretreated runoff (for the tests run during the Summer of 1994) was a composite of runoffs collected from Stafford Township, NJ, the UAB Remote Parking Lot , the Ruby Avenue Public Works Garage (Milwaukee, WI), and a metal roof (Wilsonville, AL). Runoff from the settling chamber of the MCTT at UAB Fleet Services Operation and Remote Parking Lot (corner of 8th Street South and 7th Avenue South, Birmingham, AL) was used both for the bench-scale pH/ionic strength testing and for the testing with presettled runoff (Summer 1995). Filter media columns were reconstructed after every series of tests.

Laboratory Procedures

The laboratory techniques used in this series of experiments were based upon either Standard Methods for Water and Wastewater (APHA, 1992) or on EPA-Approved Methods. The EPA-approved methods, with modifications, are described in the Quality Assurance Project Plan approved by U.S. EPA for this project (Parmer and Pitt, 1995). The modification of some methods was required in order to have more effective analyses of the stormwater pollutants. Quality assurance/quality control samples were collected and analyzed in accordance with the laboratory's approved QAPP document. Table 17 lists the chemical analyses that were conducted for each test series.

Experimental Procedure

Initial Sand Column Investigation.   This phase of testing was designed to measure the water retention and characterize the pollutant removal capability of a filter. Water retention was measured by pouring a specific volume of water through the column (300 mL) and allowing the column to drain overnight. The difference between the influent and effluent volumes of water was the water retention in the column. It was determined that approximately 50 mL of water was retained in the column for every 820 cm^3 of sand (the volume of sand in a column with inner diameter of 2.4 cm and height of 45.7 cm).

Table 17. Laboratory Analyses

	Tox	Phys. Char.[1]	Hard-ness	Solid & PSD	COD	Anion & Cation	SVOCs & Pest.	Heavy Metals
Clogging				X				
Unpretreated runoff[2]	X	X	X	X	X	X	X	X
Neutral pH, salt	X	X	X	X	X			X
Low pH, no salt	X	X	X	X	X			X
High pH, no salt	X	X	X	X	X			X
Low pH, salt	X	X	X	X	X			X
High pH, salt	X	X	X	X	X			X
PreSettled[3]	X	X	X	X	X	X	X	X

1. Turbidity, Conductivity, Color, pH.
2. Runoff: composite from NJ, WI, AL (not allowed to settle before filtration).
3. Runoff: settling chamber of MCTT (allowed to presettle for minimum of three days).

Next, stormwater runoff from one of the three Stafford Township, NJ, sites was slowly filtered through the filter in 100 mL increments. A 40-mL grab sample was collected of the effluent from each of these increments and analyzed for toxicity, turbidity, and conductivity. When the results of these tests did not agree with Austin results for their sand filters, the possibility of a lack of permanent retention of pollutants in the filter was investigated by performing mass balance analyses on the column. A calibration curve was created for a sodium chloride solution, 4 g/L NaCl, where concentration was plotted against conductivity for the filtering of the initial solution and then for washing of the filter with 18 MΩ water. These tests showed that the 'clean' water displaced any salt water that was held in the sand column pore matrix, thus confirming that flushing/displacement of trapped pollutants likely would occur in the column.

Water retention and hydraulic capacities of the newly chosen media were tested. Water flowed through the activated carbon and zeolite very quickly, which indicated that providing adequate contact time would be a problem. The peat and compost had very slow flow rates and the potential to compact, which would further decrease their hydraulic conductivities. In order to address these problems, sand was added to the adsorbent media in a 50/50 mixture by volume. This slowed the water in the 'fast' activated carbon and zeolite columns and slowed the compression of the other media. Mixing peat and compost with sand allowed channels for water flow and still provided good contact with the media, while preventing the loss of flow capacity due to compression of the media. The newly constructed columns, containing the 50/50 mixture, had more uniform hydraulic conductivities at the start of the tests. The ranking of flow rates, from highest to lowest, of the media: sand > zeolite-sand >> composted leaves ≥ carbon-sand > compost-sand > peat-sand > Enretech-sand > Agrofiber-sand. The filter fabrics, Gunderboom and EMCON, had significantly higher flow rates than any of the media.

Effect of Sediment Accumulation on Flow Rate.   The purpose of these tests was to determine the quantity of solids that could be loaded on the filtration media and fabrics before flow became 'negligible.' It included two phases. The first phase looked at the cumulative volume occupied by particles and their size distribution for both the influent (composited runoff from Stafford Township, NJ) and effluent to measure the media's ability to remove solids. The second phase was designed to determine cumulative suspended solids loading on the media using a local red, clayey soil in tap water as the influent. The total solids loading needed to cause clogging was determined from the known concentration and cumulative flow into each column. Also, the depth of red clay penetration into the column was measured visually. When the media's filtration rate slowed to less than 5 meters per day, maintenance, including breaking up any mats of the top of and in the top 2 centimeters of the filter, was done. In general, disturbance of the top of the media temporarily improved filtration rates to more than 5 m/day (but still less than 10 m/day), but continuous disturbance of the top was required. When this was no longer effective, removal of the top 1 to 2 centimeters of filter media began. Removal of the top of the media column significantly improved flow rates (to approximately 10 m/day) temporarily. During the pH/ionic strength effects tests, visible cakes of solids (approximately 5 mm thick) were removed from the top of the compost-sand column and the peat-sand column during all of the 'high ionic strength' runs. In spite of this maintenance, both of these columns clogged before the end of the respective tests and had to be removed from service. Table 18 below shows the clogging test results for the media.

Visual observation of the red clay penetration into the filter media showed the development of channels that the clayey water flowed through, thus allowing it to penetrate further into the

filter medium, yet also allowing it to avoid interacting with the top few centimeters of the media. Penetration is beneficial in that it allows for more of the filter depth to be used for treatment; however, bypassing of the media could become a problem for shallow filters. The clogging information, as it would be beneficial to stormwater filter designers, is shown in Table 19.

Table 18. Clogging Test Results for Selected Media

Filtration media	Suspended solids loading at clogging (g/m^2)	Penetration depth at clogging (cm)	Penetration depth as % of filter depth
Sand	1200-4000[a]	3.8	9
Peat-sand	200-1700[a]	2.5	5
Carbon-sand	500->2000	3.8	9
Zeolite-sand	1200->2000	5.0	11
Compost-sand	350-800	2.5	5
Enretech-sand	400-1500	2.5	5
Forest-sand	75-300	2.5	5
EMCON	3800	0.1-0.2[b]	N/A
Gunderboom	3800	0.1-0.2[b]	N/A

[a] Results from characterization of each initial media; tests not rerun.

[b] This is the height of the solids cake that formed on the top of the filter fabric, not a penetration depth into the fabric.

This effect of suspended solids' loading on the flow rate through sand is demonstrated in the figure below. As seen in the figure, even a very small suspended solids loading caused a dramatic and rapid reduction in the water flow rate through the column. However, this rapid reduction in flow capacity does not hold true once the flow rate is decreased to about 20 m/day. At that point, the curve becomes nearly flat, and filtration will continue for three-to-four times as long as the time required to reduce the flow rate to about 20 m/day.

Table 19. Treatment Capacity as Related to Suspended Solids Loading[*]

Media	Loading to 20 m/day (g/m^2)	Loading to 10 m/day (g/m^2)	Loading to <1 m/day (g/m^2)
Sand	150-450	400->2000	1200-4000
Carbon-sand	150-900	200-1100	500->2000
Peat-sand	100-300	150-1000	200-1700
Zeolite-sand	200-700	800-1500	1200->2000
Compost-sand	100-700	200-750	350-800
Enretech-sand	75-300	125-350	400-1500

* Forest-sand (Agrofiber-sand) was not tested for clogging; however, its behavior is expected to be similar to the behavior of Enretech-sand.
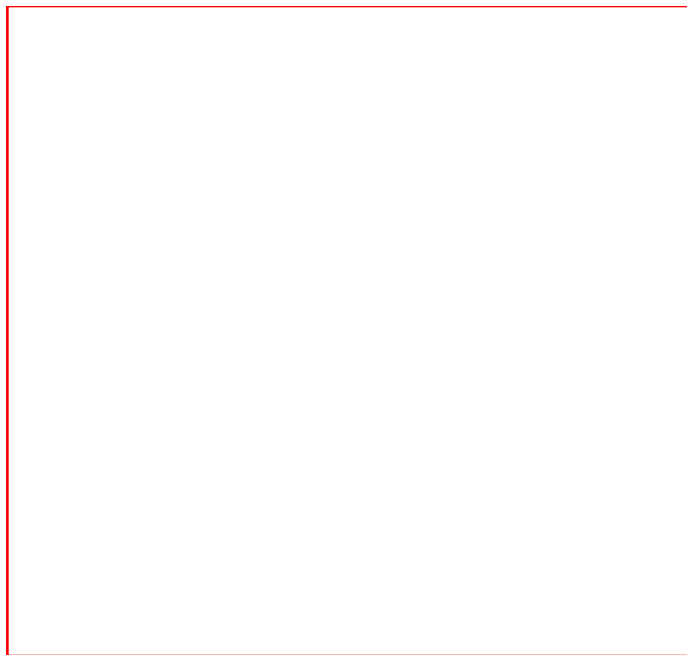
Flow Rate vs. Suspended Solids Loading on Sand

<u>pH/Ionic Strength Effect on Filtration Tests</u>.　　　　These tests were designed to determine the effects of pH and ionic strength on the ability of the filter media to capture and retain pollutants. Other researchers have shown that, for some of the media of interest, pH and ionic strength can significantly influence the ability of an adsorbent both to sorb and to permanently retain pollutants. A series of five experiments, using a full 2^2 factorial (with a midpoint) experimental design, was used to quantify the effect of pH and ionic strength on the removal efficiency and permanent retention ability of the various media. The influent was a modified runoff. The runoff was collected from the settling chamber of the MCTT. Modifications were made using an aquarium salt for ionic strength (no modification made to low ionic strength condition) and either concentrated sulfuric acid or sodium hydroxide pellets. The factorial positions were as follows:

- low pH, low ionic strength (pH $\cong$ 5, conductivity $\cong$ 200 μS/cm)
- low pH, high ionic strength (pH $\cong$ 5, conductivity $\cong$ 10,000 μS/cm)
- high pH, low ionic strength (pH $\cong$ 9, conductivity $\cong$ 200 μS/cm)
- high pH, high ionic strength (pH $\cong$ 9, conductivity $\cong$ 10,000 μS/cm)
- neutral pH, medium/high ionic strength (midpoint – pH $\cong$ 7, conductivity $\cong$ 8,000 μS/cm)

Six grab samples then were captured periodically during each filter run (corresponding to hydraulic loadings on the columns of 1.9, 3.6, 5.2, 6.9, 8.8, 11.6 m (m^3 water/m^2 filter area)). The samples were analyzed for the parameters listed in Table 17. Additionally, flow rate and cumulative water volume passing through the filter were noted. Statistical analysis of this data was performed by two independent methods. A one-tailed Wilcoxon sign-rank analysis (procedure described in Lehmann, 1975) was used to test the hypothesis that filtration would not significantly change the influent concentration for the parameter of interest. P values less than 0.10 are considered significant and lead to the conclusion that filtration significantly affected the influent concentration of a given parameter. The weakness of this test as it was run is that the P values do not indicate whether the significant changes that occurred during filtration were a reduction or an increase in a parameter's concentration. The second statistical test performed was a factorial analysis for the four bench-scale tests where both pH and ionic strength were modified. The detailed procedure for performing the factorial analysis is given by Berthouex and Brown (1994) and for interpreting the results is given in Box, Hunter and Hunter (1978). In general, pH, ionic strength, or the interaction of the two were considered significant when the calculated effect for

each influence was greater than three times the group standard error. Factorial analysis was performed on two sets of results for each parameter: the effluent concentrations, and the removal efficiency, measured as percent decrease, in a constituent due to filtration.

Clogging was affected by changes in pH and ionic strength. The changes in pH and ionic strength also affected the permanent retention of the pollutants in the columns after the tests. No chemical breakthrough was noted for any of the tests during the test durations; the columns clogged and ceased to allow filtration before their chemical removal capacity was exceeded. Clogging of the peat-sand filter occurred during the neutral pH, high ionic strength run, but not during the other runs (except at the end of the high pH, high ionic strength run), indicating that filtering influents with high conductivities will reduce the life of the filter, while either a significantly acidic or alkaline influent will tend to prolong the filter run. The clogging of the compost-sand filter during both the high ionic strength tests (low and high pH) indicates that filtering influents with high conductivities will reduce the life of the filter, and, unlike peat, a significantly acidic or alkaline runoff does not appear to prolong the life of the filter.

Long Term Filtration Tests. Long-term performance information is crucial in designing filters for any application because it determines the required maintenance schedule. One criteria for a good stormwater filter will be the lack of regular maintenance. The 'unpretreated runoff' tests used water that was a composite of runoff from six locations: UAB Remote Transportation Parking Lot, UAB Lot 15 Student Parking Lot in front of the Engineering Building, Ruby Avenue Public Works Garage, and three sites in Stafford Township, NJ. During filtration, the influent water to the columns was stirred regularly to ensure that very few solids could settle out on the bottom. Significant reductions in flow rate were observed after 5.5 m of runoff had been filtered. The 'presettled runoff' tests used water that had been collected in the settling chamber of the MCTT at least three days prior to the test date. Because the suspended solids in the presettled water were colloidal, retention of solids was not observed for any of the media even after the fifth storm event although the significant decreases in flow rates indicated physical retention of solids.

All columns were rebuilt prior to the start of both sets of long-term filtration tests. However, the columns were not cleaned out and rebuilt between the storm events in order to examine pollutant removal and retention under typical, long-term usage. Composite samples were collected of the effluent from each designated 'storm event' and were analyzed for the constituents listed in Table 17. Some samples were split into filtered and unfiltered fractions in order to evaluate the fate of each in the filters, since it was expected that it would be different. Clogging occurred when the 'unpretreated' was used as the influent. This is the reason that the influent water was allowed to settle for three days after collection for the last set of long-term filtration tests. It was felt that this would allow chemical capacity to be monitored more effectively, since physical clogging would not occur so early in the run.

A Wilcoxon sign-rank analysis was used to test the hypothesis that treatment did not significantly change the concentration of a given parameter. P values less than 0.10 were considered significant and led to the conclusion that treatment did significantly change the concentration of a parameter during passage through the column. However, this P value does not indicate whether or not a specific media removed the parameter of interest or leached out more of that parameter. Therefore, P values that indicate statistically significant removals are in italics in the tables. For those parameters where both the unfiltered and filtered fractions of a sample were analyzed, Wilcoxon sign-rank P values were calculated for both sample fractions. Statistically significant pollutant removals are shown in Table 20.

Pretreatment of the water by settling for a minimum of three days to significantly reduce the suspended solids increased the water volume that could be treated before clogging. However, it generally decreased the amount of sediment needed to clog the media columns. The settling pretreatment removed all of the faster-sinking particles (generally the largest particles), leaving the smaller and less dense particles in the solution. These particles appeared to have a greater detrimental effect on the media than the larger and more dense particles.

The activated carbon showed the greatest pollutant concentration reductions compared to the other media. The removal capability seemed to slightly decrease with time; however, there was no indication that chemical breakthrough had been achieved for this medium. The other media did not show as great an adsorption ability as the activated carbon and generally contributed more undesirable constituents to the effluent. The Enretech-sand, Forest-sand, and the filter fabrics had the poorest removal efficiencies of all the media. They were only capable of significantly removing between three and five parameters. The compost-sand also was not effective at removing many constituents from the influent. The zeolite-sand medium was only slightly better than the sand medium for the number of potential pollutants that it removed. The compost-sand and peat-sand media showed significant increases in organics in their effluents due to the natural humics that are washed off the media during treatment.

Table 20 summarizes the results of the long-term tests by giving average percent removals during treatment for those media which had significant reductions in the influent concentration of a parameter. The results are given for each parameter for the presettled influent first and then the normal influent that was not presettled. An entry of "*" means that the media made no significant reductions in that parameter during treatment. Parameters that are not listed had no media that caused a significant removal during treatment.

Table 20. Average Percent Removal by Media

	Carbon-sand	Peat-sand	Zeolite-sand	Compost-sand	Enretech-sand	Forest-sand	Sand	Gunderboom	EMCON
Physical characterization									
Toxicity (U)	*/100	*/*	*/87	*/100	*/<10	*	*/*	*/*	*/*
Toxicity (F)	83/95	63/61	100/45	*/71	*/*	*	*/*	*/*	*/*
Color (U)	*/60	*/*	*/*	*/*	*/*	*	*/*	*/*	*/*
Color (F)	26/64	*/*	*/*	*/*	*/*	*	*/*	*/*	*/*
Major anions									
Carbonate	47/69	100/87	*/*	*/*	*/*	*	*/*	*/*	*/*
Bicarbonate	23/44	*/*	*/*	*/*	*/*	*	*/*	*/*	*/*
Fluoride	*/*	*/<10	*/*	*/*	*/*	*	*/*	*/*	*/*
Chloride	*/*	17/*	7/*	*/*	*/*	*	*/*	*/*	*/*
Nitrate	97/94	*/*	*/*	*/*	*/*	*	*/*	*/*	*/*
Sulfate	*/*	5/*	*/*	*/*	*/*	*	*/*	*/*	*/*
Major cations and hardness									
Hardness	*/*	52/59	*/*	*/*	*/*	*	*/*	*/*	*/*
Potassium	15/46	*/*	39/35	*/*	*/*	*	*/*	*/*	*/*
Calcium	*/*	88/75	17/*	*/*	*/*	*	*/*	*/*	*/*
Solids and particle size distribution (PSD)									
Total solids	*/*	27/*	*/*	*/*	*/*	*	*/11	*/10	*/5
Diss. solids	*/*	45/*	*/*	*/*	*/*	*	*/*	*/*	*/*
Susp. solids	*/52	*/*	*/45	*/*	*/*	*	*/74	*/31	*/23
Vol. solids	*/71	*/*	*/17	*/*	20/*	*	8/20	*/<5	*/*
VDS	*/59	*/*	*/*	*/*	*/*	*	*/*	*/*	*/*
VSS	*/85	*/*	*/33	*/*	*/*	*	*/*	*/*	*/*
Cum. PSD	*/81	*/28	*/58	*/27	*/*	*	*/65	*/*	*/*
Metals									
Zinc (U)	76	70	73	76	66	77	77	*	*
Zinc (F)	48	58	62	82	77	81	81	*	*
COD (U)	96/*	*/*	*/*	*/*	*/*	*	*/*	55/*	22/*
Chemical oxygen demand; semi-volatile organics; and pesticides									
COD (F)	85/59	*/*	*/*	*/*	*/*	*	*/*	*/*	*/*
2,4-DNP	43	36	*	*	30	*	*	79	*
DnBP	*	66	*	*	*	*	*	76	*
B(2eh)P	90	23	82	*	*	*	94	*	*
PCP	*	*	79	*	87	92	100	*	*
Dieldrin	*	68	*	*	*	*	*	*	*

NOTES: * No significant removal occurred. / Divider between long term tests. PreSettled/unpretreated average removal in table.

U Unfiltered fraction of runoff. F Filtered fraction of runoff.

VDS Volatile dissolved solids. VSS Volatile suspended solids.

PSD Particle size distribution (1 to 128 μm). COD Chemical oxygen demand.

2,4-DNP 2,4-Dinitrophenol. DnBP Di-n-butyl phthalate.

B(2eh)P Bis(2-ethylhexyl) phthalate. PCP Pentachlorophenol.

Conclusions Regarding Selection of Filtration Media

The selection of the filter media needs to be based on the desired pollutant removal performance and the associated conditions, such as land use. If the selection criterion is only suspended solids removal and using normal stormwater that is not pretreated (most common), then the filtration media would be ranked according to the following (bench-scale testing results, which may differ, reported in parentheses):

- >50% reduction for suspended solids: Sand and carbon-sand (both long- term and bench-scale testing indicated these high suspended solids reductions)
- 20-50%:   Zeolite-sand and filter fabrics (long-term testing; bench scale removals: >90% zeolite-sand, <10% filter fabrics)
- <10%:   Peat-sand and Enretech-sand (long term testing; bench scale removals: 80-90% peat-sand, >90% Enretech-sand)

If the filter media were being selected based upon a wider range of pollutants for normal stormwater that is not presettled, then the ranking, based on the number of pollutants that would be removed during filtration, would be as follows (with additional comments pertaining to degradation by other pollutants in parentheses):

- Carbon-sand (minimal to no degradation of effluent)
- Peat-sand (degradation of effluent with higher turbidity, color, COD, small particles)
- Zeolite-sand and sand (minimal degradation of effluent)
- Enretech-sand (minimal degradation of effluent)
- Compost-sand (degradation of effluent with higher color, COD, solids)
- Forest-sand and filter fabrics (minimal degradation of effluent)

All of the filters perform better after they are aged because they have the potential to build up a biofilm that will aid in permanent retention of pollutants. Aged filters also have fewer small particles that may be available to be washed out of the media during filtration.

There are other additional problems that the stormwater filter designer must recognize. When selecting a media, the designer must remember that most of these media are ion-exchange materials. This means that when ions are removed from solution by a filter medium, then other ions are released into solution. In most instances, these exchangeable ions are not a problem in receiving waters, but the designer should know what is being added to the water. For this activated carbon, the exchangeable ion is mostly sulfate; while for the compost, the exchangeable ion is usually potassium. The zeolite appears to exchange sodium and some divalent cations (increasing hardness) for the ions it sorbs. Another potential problem caused by stormwaters entering receiving waters is eutrophication due to the loading of inorganic nitrogen, phosphate, or both into the water. Only the activated carbon was capable of effectively removing nitrate from the runoff. Phosphates, which are a greater problem in most areas of the country, were not present in the runoff that was tested, and, therefore, no judgments can be made about the ability of these media to remove phosphate from the water. The most restrictive materials (the Enretech and Forest Products media) are very fibrous and, even when mixed with sand, they still show some compaction. The most granular media (activated carbon and zeolite) are relatively uniform in shape and size but are very large when compared to the sand grains. Sand was used with the carbon and the zeolite to reduce the water's flow rate through the media to increase contact time for better pollutant removal. The sand has the highest filtration rate because it has the most uniform shape and size.

Presettling of the stormwater runoff had a significant effect on filter performance, and the rankings would be as follows, using a wide range of stormwater pollutants. Since the suspended solids concentration is not likely to be further reduced by the filters, it by itself would no longer be a suitable criterion for selecting a medium.

- Carbon-sand (minimal effluent degradation)
- Peat-sand (degradation of effluent color, turbidity, pH)
- Zeolite-sand, Enretech-sand, Forest-sand, sand (min. effluent degradation)
- Compost-sand (minimal removal, color degration)
- Filter fabrics (minimal improvement or degradation)

Obviously, the stormwater control objectives and options will significantly affect the selection of the media. This is most evident with the compost media. If suspended solids removal alone is the criterion, and if one can live with a slight color increase, then the compost filter is a good choice for an unpretreated stormwater. However, if the filter is to be used after significant pretreatment, the compost filter then is not a very good choice.

The following paragraphs are summaries of the likely significant reductions in concentration for the filters. This list also includes the minimum expected effluent concentrations for suspended solids, color, and turbidity.

Sand.   The sand filter will provide moderate to good removal for many pollutants that are associated with the particulates and has a greater removal efficiency when the stormwater is not presettled. When the influent was presettled, significant removal only occurred for volatile total solids, zinc, and two of the organics, bis(2-ethylhexyl) phthalate and pentachlorophenol. Influent pH and ionic strength, acting independently, can affect both the final effluent quality and removal efficiency with the highest effluent zinc, suspended solids, and COD concentrations occurring when the influent pH was low and the influent salt concentration was high.

For the sand filter, the level of control available for any parameter is associated with the retention of suspended solids and the associated particulate fractions of pollutants. The sand filter can flush out previously captured pollutants until the filter is aged and a biofilm is grown that will more permanently retain pollutants. When the water is presettled, little removal benefit occurs. The likely minimum effluent concentrations are as follows: 10 mg/L for suspended solids, 50 HACH color units, and 10 NTU for turbidity.

Peat-sand.   The peat-sand filter provides moderate to excellent pollutant control for most pollutants for both normal and presettled stormwater runoff. In general, the best average removal efficiency occurred for presettled runoff. The disadvantage of the peat-sand filter is the increase in turbidity and color in the effluent and the reduction in the pH of approximately one to two pH units. The influent pH and ionic strength will control both the effluent quality and removal efficiency. Low influent pH causes a poorer effluent quality for hardness, zinc, copper, and color. High influent pH leads to higher effluent COD concentrations. The influent ionic strength controls the effluent turbidity and zinc.
Unlike the sand filter, the peat-sand is capable of removing pollutants immediately by either sorption or ion-exchange. Presettling of the runoff prior to filtration appears to improve the removal ability of the filter. The drawback to the use of the peat-sand filter is the addition of turbidity and color to the effluent. Color and turbidity can be expected to be added to the filter every time that the filter goes dry, which will occur regularly for most stormwater filters. The expected minimum effluent concentrations for the peat-sand filter would be 5 mg/L for suspended solids, 85 HACH color units, and 10 to 25 NTU for turbidity.

Activated carbon-sand.   The carbon-sand filter provides good to excellent control for many pollutants, especially if the stormwater is not presettled. The carbon-sand filter does not have as good a removal efficiency when the effluent has been allowed to settle for several days. The influent pH and ionic strength will affect the effluent quality and removal efficiency for this filter. The interaction of these two parameters controls the effluent COD and toxicity, and the influent ionic strength controls the turbidity and the color. The influent pH appears to have the greatest effect on metals removal, with the greater removal efficiency and best effluent quality occurring when the pH is above neutral. The addition of salt to the influent positively influences the effluent turbidity but provides a negative influence on the effluent toxicity, color, and chemical oxygen demand.

The carbon-sand filter is also capable of removing pollutants immediately upon use through either sorption or ion-exchange. The carbon tested in these experiments uses sulfate as its exchangeable ion. A new carbon filter, however, will wash the carbon black dust out of the filter during the first couple of washings, and there may be a slight increase in turbidity for the first two or three storms if the runoff is presettled prior to filtration. The expected minimum effluent concentrations are 5 mg/L for suspended solids, 25 HACH color units, and 5 NTU for turbidity.

Zeolite-sand.   The zeolite-sand filter provided moderate-to-good removal for several pollutants when the runoff was not allowed to settle prior to filtration. However, removal efficiency was not as good and only occurred for fewer parameters when the runoff was presettled. Because the zeolite particles were very large (2 to 5 mm in diameter), the possibility exists that channels were formed in the media, and the runoff flowing through the channels did not have sufficient contact time with the media. The influent pH and ionic strength controlled the effluent toxicity, turbidity, chemical oxygen demand, and zinc. When the influent salt concentrations were high, the effluent turbidity and color were lower (compared to the effluent from the low salt influent conditions), but more hardness was added to the effluent.

The zeolite-sand mixture was expected to provide better removal than was shown in these experiments. However, if channels were present in the media and the underlying sand layer did not provide sufficient retention of water in the mixed zeolite-sand layer, then adequate contact time may not have been available for pollutant removal. The other problem with this zeolite is that it was designed for ammonia removal, and the pore size may not have been large enough to encourage removal of a wider variety of pollutants. The expected minimum effluent concentrations are 10 mg/L suspended solids, 75 HACH color units, and 15 NTU for turbidity.

Compost-sand.   The compost-sand filter provided moderate-to-excellent removal of many pollutants when the runoff was not presettled. However, when the runoff was presettled, the compost-sand did little to improve water quality and worsened the color, hardness, and chemical oxygen demand of the effluent. Like the other sorption and ion-exchange media, heavy metals removal was good in this media even for presettled runoff. The influent pH and ionic strength interacted to control the effluent quality and removal efficiency for hardness, chemical oxygen demand, zinc, and copper. For the metals, the poorest effluent quality occurred when the pH was low and the salt concentration was high. The addition of salt to the influent caused more hardness to be present in the effluent than when the runoff's salt concentration was not adjusted.

The compost-sand mixture has the ability to remove pollutant immediately upon use. However, like the peat-sand filter, when the filter goes dry between storms, color-producing organics are likely released from the medium and retained in the pores, waiting to be washed out during the next filtration. Also, the potential exists to wash solids from the media that are small enough to avoid being trapped during passage through the underlying sand filter. The minimum expected effluent concentrations for the compost-sand filter are 10 mg/L for suspended solids, 100 HACH color units, and 10 NTU for turbidity.

Enretech-sand.   The Enretech-sand filter provided moderate control for several pollutants in untreated runoff, but it had little pollutant removal ability when the runoff was allowed to settle for several days. Low influent pH caused an increase in the effluent hardness while a high influent ionic strength caused the poorest effluent chemical oxygen demand. The interaction of pH and ionic strength controlled the removal of the heavy metals. The minimum expected effluent concentrations for the Enretech-sand filter are 10 mg/L for suspended solids, 80 HACH color units, and 10 NTU for turbidity.

Forest-sand and Filter fabrics.   The Forest-sand filter provided little removal with the exception of the heavy metals. The filter fabrics were capable of removing suspended solids from the runoff and pollutants associated with those solids. Of the filter fabrics tested, the Gunderboom provided the best overall removal capability. It would be an excellent choice for use as the top layer for gross solids removal.

The test observations indicated that only about 2.5 cm of the filter columns (about 10% of the column depth) were actually used for solids retention during these tests. It is assumed that a full-scale filter could use about 5 times these depths for solids retention if careful, selective piping to deeper depths, while preventing short-circuiting of the entire filter, was allowed. The Metropolitan Washington (D.C.) Council of Governments recommends placing a turf grass layer on top of the media where the roots of the grass would cause channel development through the top layer only (Galli, 1990). They recommend that the roots of the grass cover do not extend below about one-half the filtration depth (up to approximately 12 cm). Mechanical removal of the clogged layer to recover filter flow rates was not found to be very satisfactory during this research, but it has been used successfully during full-scale operations. Great care must be taken when removing this layer since loosening the media may enable trapped pollutants (associated with the suspended solids) to be easily flushed from the media.

The flow rates through filters that have been thoroughly dried between filter runs are significantly increased when compared to the flow rates prior to drying. The small-scale tests run here restricted complete drying during normal inter-event periods. Drying may occur more frequently in full-scale filters. Wetting and drying of filters (especially peat) has been known to produce solution channels through the media that significantly increases the flow. If these solution channels extend too far through the filter, however, the runoff may bypass part of the media and removal efficiency will be decreased. Table 21 shows the observed increases in filter flow rates for saturated (and partially clogged filters) and the associated flow capacity recovery for filters that have been thoroughly dried and then re-wetted.

Table 21. Filter Flow Rates (m/day) for Saturated and Partially Clogged Filters
and Recovered Filtration Capacity after Thorough Drying

Filter media	Saturated/partially clogged	Recovered flow capacity after drying	Flow Increase (multiple)
Sand	13	40	3.1 X
Peat-sand	4	42	11 X
Carbon-sand	17	33	1.9 X
Zeolite-sand	17	39	2.3 X
Compost-sand	13	32	2.5 X
Enretech-sand	8.4	24	2.9 X
Forest-sand	8.4	17	2.0 X
EMCON fabric	850	850	1.0 X
Gunderboom fabric	200	200	1.0 X

The filter fabrics did not indicate any flow-rate improvements with wetting and drying. As expected, the peat-sand filter had the greatest improvement in flow capacity (by about ten times). The other media showed more modest improvements (but still about a two to three times increase in flow rate).

The above filter capacity ranges are associated with varying test conditions and may be further grouped into the approximate categories shown in Table 22. A multiplier of five was used to account for the greater anticipated filter flow capacity associated with full-scale operations.

Table 22. Filter Categories Based on Capacity

Capacity to <1 m/day (gSS/m^2)	Capacity to 10 m/day (gSS/m^2)	Filtration media in category
5,000	1,250	Enretech-sand; Forest-sand
5,000	2,500	Compost-sand; Peat-sand
10,000	5,000	Zeolite-sand; Carbon-sand
15,000	7,500	Sand

CHAPTER 9: DISSERTATION RESEARCH PROJECT DESIGN

Introduction

The overall goal of this project is to further the evaluation of the potential for using filtration media to treat stormwater runoff, especially stormwater runoff from areas where pollutant loadings are expected to be greater than normal. Specifically, this project will investigate several natural and synthetic media to determine both their applicability and their appropriateness for use in stormwater treatment (including potential future maintenance and disposal problems). Natural media, especially, are of interest because they usually are low cost and readily available. Also of interest are potential waste materials, such as a cotton textile waste, which are currently being landfilled. The purpose of this research is twofold: first, to investigate the effects of different influent water characteristics on the removal capacity of the various filter media during column operation and, second, to evaluate the filter media using a pilot-scale device and an influent of pre-settled stormwater runoff.

In general, filter performance is measured by effluent water quality (traditionally, turbidity and suspended solids concentration, possibly particle counts and dissolved organic carbon concentration [DOC]), heavy metal concentration (where applicable), water production (unit filter run volume), and head-loss development (rate and time to back wash), all of which change over time. Filtration performance depends on the source water quality (types and concentrations of pollutants), any required chemical treatment, and the physical characteristics of the media (type, size distribution, depth, and hydraulic loading rate) (Clark and Pitt, 1998). Filters for water purification have traditionally been sand or a dual media (sand and anthracite). Pure sand has minimal adsorption capacity; however, amending the sand with iron oxide and/or promoting a biofilm growth will significantly enhance sand's removal efficiency. Sand's removal efficiency has also been improved by mixing it with an organic media that has good pollutant removal capabilities. Good ion-exchange or sorption media will have a high organic content (or be inorganic with a high surface charge), a high cation exchange capacity (CEC), and a neutral to alkaline pH. This work assignment will investigate, using actual stormwater runoff, the effectiveness of various natural media for storm water filtration. The media, in addition to sand, which will be investigated as part of this project include the following:

- Activated carbon

- Zeolite for ammonia removal

- Peat moss

- Municipal leaf-based compost

- Cotton Textile Waste

- Shredded kenaf fibers

- Topsoil (only used in the pilot scale device)

- Lightweight sand (only used in the pilot scale device)

The potential for using filtration media to treat stormwater runoff was investigated under a Cooperative Agreement between the Environmental Protection Agency (EPA) and the University of Alabama at Birmingham (UAB) (Cooperative Agreement Number CX824933). The results of that project indicated that filtration/sorption media are potentially useful for treating stormwater runoff. However, there are still many questions that could not be answered under the scope of that project. These questions specifically included the development and evaluation of design equations that accounted both for the chemical capacity of the media and the need for maintenance due to potential physical clogging and/or use of the available chemical capacity. Also, since all of the prior work was performed using laboratory-scale setups, it is unknown exactly how the filters will perform under normal field conditions.

One of the concerns raised during the laboratory work is short-circuiting/bypassing of the filter media. The literature indicated that, as long as the width/diameter of the filter surface was greater than 20 times the average grain size, wall effects such as short-circuiting should not be a concern. The filter diameter was approximately 100 times the average grain size (filter diameter =45.3 mm, average particle size = 0.45 mm). However, some of the results (particularly the solids) from the prior laboratory work indicated that bypassing of the filter media may be occurring. A second problem with the small columns used in the laboratory work was that the complete depth of media never completely dried out (not even after being out of use for several months). While it is not expected that filters in the field will dry completely (interevent period for Birmingham: 3 days average, range of <1 day to 14 days), it is expected that, in a pilot-scale device, the top and bottom several inches will dry. This drying cycle is expected to affect filter performance, including increasing flow rate in a slow-flowing filter. The cycle of wetting and drying of the filter also will affect the growth and particularly composition of any developing biomass. The organic filters should provide an excellent substrate for bacterial growth, while the other filters may provide an acceptable one. In order to more accurately predict actual performance and to clarify design questions, pilot-scale setups will be required.

The overall goal of this project will be pursued by investigating the following:

- Suspended solids loading needed to clog the filters (for design).

- Contact time, ionic strength, and pH effect on pollutant removal and retention.

- Effect of anaerobic conditions on the filter's ability to retain captured pollutants.

- Performance of pilot-scale filter columns for treating intermittent flows of stormwater runoff.

The results of this project will be used in conjunction with work being funded by U.S. EPA Urban Watershed Management Branch on jute and mulch media. The results also will be used in conjunction with work funded by Water Environment Research Federation regarding the capacity of the media for the metals and organics typically found in stormwater runoff, and the equilibrium and kinetic parameters of the various media for sorption of metals and organics.

Modeling of the Stormwater Filtration Process

Filtration, especially 'slow filtration,' is of interest to designers of best management practices (BMPs) for stormwater treatment because filters will work on intermittent flows without a significant loss of capacity and their placement is flexible. Underground placement of and/or retrofitting underground stormwater filters is possible in many locations, thus allowing the complete aboveground area to be developed. However, in order for this form of treatment to be effective and accepted for use, design equations/modeling algorithms that account for all the processes occurring within the filters must be developed. In a stormwater filter, two major processes are occurring: (1) the physical removal of particulate pollutants from the water by straining the water and trapping the solids in the pores of the media, and (2) the chemical binding reaction between the pollutants and the surface of the media, i.e., adsorption/ion-exchange. Investigators have been examining the pollutant straining mechanism for many years in water treatment and wastewater treatment filters and have developed design equations for predicting the pollutant removal ability of a filter over time for these continuous flow applications. Also, for many years, the adsorption/ion-exchange process has been investigated

and modeled both on a macro- (filter)-scale and on a microscale, e.g., looking at the adsorption of solutes onto individual sorbent particles. However, these adsorption investigations have primarily been concerned with the separation of a product from a waste stream and the treatment of industrial wastewater. These traditional applications typically involve very high influent concentrations of the chemical(s) of concern and tend to have a matrix that, once characterized, will tend to be somewhat predictable in terms of constituent concentrations and impacts on the adsorption process. The influent water to a stormwater filter, unless preceded by a detention pond, may be variable, and will depend on the magnitude of the dry and wet weather discharges, the length of the antecedent dry period, the intensity of the rain, the surface characteristics of where the pollutant is located, and site-specific conditions that cause pollutant accumulation (Pitt, et al. 1995). In order for filtration to become a useful treatment technique, the design will need to be sufficiently robust to cope with the variety of conditions that could be seen during the life of the filter. The major difference for the sorption process between the traditional applications and the application to treat stormwater is the significantly lower concentration of most of the pollutants in stormwater runoff.

The following are brief descriptions of the method proposed by Urbonas (1999) to predict flow rate in a filter loaded with suspended solids and of the methods used to design a traditional fixed bed adsorber. The research proposed here will include the development of the modeling algorithm that can be used to predict treatment efficiency and life of stormwater filters and the evaluation of the algorithm to predicting chemical breakthrough during non-neutral influent pH and ionic strength conditions. Also, the algorithm will be used to predict physical and chemical breakthrough in pilot-scale filters that are treating pre-settled stormwater runoff. These modeling results will be compared with the experimental data to determine the effects of the changing influent conditions and of scale-up on the model coefficients, and to determine the differences in the ability of the different filtration media to effectively treat stormwater.

Particulate Removal Modeling

Urbonas (1999) developed a series of design equations that can be used to predict the unit flow rate through the filter based on the suspended solids load and to estimate the required size (surface area) of the filter based on the required removal capacity per area of filter and on the maintenance interval predicted for the filter. For a sand filter, the suggested design equation for predicting the unit flow rate, q, through the filter in feet per day (ft^3/ft^2-day) based on the suspended solids load, L_m, accumulated on/in the filter in pounds per square foot of filter area is the following:

$$q = k_i \bullet L_m^{-c} \qquad\qquad\qquad [1]$$

or for the sand filters:

$$q = 1.50 \bullet L_m^{-1.165} \qquad\qquad\qquad [2]$$

Although Urbonas developed these equations for the sand filters installed in Lakewood, Colorado, Equation 1 above can be used to model the suspended solids removal for any site for any filter medium. This research will include the development of clogging curves (flow rate versus suspended solids loading) for each of the media. Based on previous work, it is anticipated that equation (1) can be used to predict the decreased flow rate through the media as the suspended solids loading on the media increases. The coefficients calculated for each filtration media and column set-up can then be statistically compared (description of statistical work provided later) to see if the choice of media significantly affects the clogging of the filter.

Sorption Capacity Modeling

While physical straining of particulate constituents is occurring in the filter, removal of the dissolved pollutants by adsorption/ion-exchange also may be occurring. When a mass of adsorbent and a waste stream are in contact for a sufficiently long time, an equilibrium between the amount of pollutant adsorbed and the amount remaining in solution will develop. For any system under equilibrium conditions, the amount of material adsorbed onto the media can be calculated using the mass balance of Equation (3):

$$[3]$$

where X/M = mass of pollutant per mass of media [typically expressed as mg pollutant/g media], C_0 = initial pollutant concentration in solution, C_e = concentration of the pollutant in

solution after equilibrium has been reached, V = volume of the solution to which the media mass is exposed, and M = mass of the media.

Isotherm adsorption models have been used in waste stream treatment to predict the ability of a certain adsorbent to remove a pollutant down to a specific discharge value. The two commonly used isotherm models are the Langmuir and the Freundlich models (Cooney 1999; McKay 1996). The general Langmuir equation is:

[4]

The Langmuir isotherm can be linearized to the following equation:

[5]

From the linearized form of the Langmuir isotherm, the isotherm constants, K_L and a_L can be determined using linear regression.

The general form for the Freundlich model is:

[6]

The Freundlich isotherm can also be linearized by the following:

[7]

Breakthrough Curve Theory

The Langmuir and Freundlich isotherms are only applicable to batch adsorber systems where sufficient time is provided to allow equilibrium between the pollutant in solution and the pollutant adsorbed on the media to occur. Many applications of adsorbers to waste streams use a fixed-bed approach where the waste stream flows through a stationary mass of adsorbent. During the flow through the adsorbent, many of the pollutants are expected to come into contact with active surface sites and thus be retained on the surface of the adsorbing media through either physisorption or chemisorption. The design of these fixed adsorbers requires the determination of two significant design parameters: minimum contact time and capacity of the bed.

The minimum contact time is determined through a series of kinetics tests in which a known mass of media is exposed to a polluted waste stream of known concentration for specific amounts of time. At the end of each time increment, the concentration of the pollutant in the solution is measured and the ratio of the final concentration to the initial concentration is plotted against time. The time at which the curve begins to flatten is the minimum contact time required for the development of a pseudo-equilibrium. Although removal may continue past this minimum time, longer contact times in general are not economically efficient because the size of the adsorber will need to be much greater for minimal additional removal.

The service life of the bed can be determined using the bed depth-service time [BDST] model, which is based on the Bohart and Adams "quasi-chemical" rate law (Cooney 1999). The assumption behind the Bohart and Adams equation (Bohart and Adams 1920) is that equilibrium is not instantaneous and therefore, the rate of the sorption reaction is proportional to the fraction of sorption capacity still remaining on the media. The linearized BDST model equation is as follows (Cooney 1999; McKay 1996):

[8]

where t_b = time until breakthrough (min)

       C_0 = initial concentration of pollutant (mg/L)

       C_b = breakthrough concentration of pollutant (mg/L)

       v = fluid velocity or loading rate (m/min)

       ε = porosity of the filter

> k = quasi-chemical rate constant from Bohart and Adams theory (L/mg-sec)

> N_0 = capacity of the media for each pollutant in a multi-component solution (mg pollutant per cubic meter of filter volume)

> D = depth of the filter bed

The '1000' is included in the above equation as the conversion factor between liters and cubic meters, i.e., 1000 L per cubic meter.

The parameter N_0 will be estimated from a multi-component equilibrium study where a small mass of each medium will be exposed to a large volume of presettled stormwater runoff spiked with standards and whose final concentration will reflect the upper end of the typical concentrations of metals and nutrients found at the source areas where these filters would be typically deployed (approximately 0.5 mg/L copper, lead, zinc, nitrate, ammonia, and phosphate).

The rate constant, k, will be estimated from the contact time/kinetics studies described later. The data from the plots of the ratio of effluent concentration to influent concentration versus exposure time can be regressed using the form:

$$[9]$$

The constant a should be approximately 1 for the Bohart and Adams theory of applying a 'quasi-chemical' rate law to sorption to be valid, i.e., where the driving force for the sorption is the difference in the amount of pollutant sorbed to the media and the capacity of the media for the pollutant. This k is a 'lumped parameter' rate constant and does not attempt to identify and quantify the effect of the rate-limiting step on the sorption process. The BDST model is then called a 'lumped-parameter' model. Its simplicity makes the investigation of its practicality for stormwater filter design desirable.

Combining Physical and Chemical Removal in a Single Series of Design Equations

The final algorithm for a stormwater filter design must incorporate both the physical straining and the chemical 'adsorption' occurring in the filter. Breakthrough for a filter will need to be defined by the designer. In general, it will be defined as the time at which either the effluent concentration of one of the pollutants has exceeded the design criteria, often a regulatory concentration limit, or when the flow through the filter is reduced to the point below which it is not acceptable, i.e., when either most of the flow bypasses the filter or, if bypassing is not possible, the water accumulates to an undesirable depth in an undesirable location.

The two choices for the design modeling include the use of models that have already been developed or the development of the algorithm that will calculate breakthrough based on either of the criteria described above. Both of these approaches will be investigated as part of this research. Two or three existing one-dimensional solute transport models (preferably ones where the influent flow rate can be modified throughout the run to simulate the physical clogging of the media that will occur) models will be examined to determine their potential applicability for describing stormwater filtration. Based upon a review of the models offered by U.S. EPA, the U.S.G.S., and the Army Corps of Engineers through their web sites and the links provided therein to software providers, it is anticipated that the models investigated as part of this research will be those used in one-dimensional groundwater and vadose zone modeling. VLEACH, GMS and HELP are the three models proposed for review of the one-dimensional transport of pollutants through a filter column. The concern with these models is that they are not capable of accounting for the loss of flow and increase in head loss as the suspended solids accumulation in the medium increases. The second concern with these models is that the input demanded may not be feasible to obtain by stormwater filter designers.

An algorithm/design equations for pollutant removal (both dissolved and particulate forms) and clogging potential, will be developed once the capacity and rate constants have been calculated. This algorithm will be applied to both the pilot-scale and to the laboratory breakthrough curve data. The coefficients for the modeling equations will be compared statistically to determine if the results of the laboratory tests can be used to adequately predict pollutant removal in the field, especially under non-neutral influent pH and ionic strength conditions.

Determination of the Required Number of Samples

The first step in designing any experiment is the selection of the appropriate statistical hypothesis. Statistical hypotheses are different from what might be expected. The idea is to

disprove a null hypothesis (say that the probability of the null hypothesis [designated H_0] occurring is less than a certain P value). This then leads to the acceptance of the alternative hypothesis (designated H_1). Acceptance of the null hypothesis, however, means that there is not sufficient evidence to refute it. The null hypothesis might be true or possibly, the sample size is too small to provide a statistically meaningful result. For example, in prior testing of the filters on a laboratory scale, the experimental design called for the collection of five influent and five effluent samples for each filter. This number of samples was expected to be sufficient to see significant differences ($p < 0.05$) in influent and effluent concentrations when the percent pollutant removal was 50% with an acceptable coefficient of variation of 50%. Significant differences in influent and effluent concentrations could be seen for most pollutants if they existed. However, changes in the semi-volatile organic concentrations (base-neutral and acid extractable organics as analyzed by EPA Method 625) during filtration could not be found to be significant to the 0.05 level because the frequency of detection of a compound was less than 50% and therefore the number of paired sample results was too small to give a probability of significant removal of less than 0.05.

Because this hypothesis testing is based on the idea that the probability of the null hypothesis being true is less than a pre-specified value, designated α, the possibility exists that rejection of a true null hypothesis or acceptance of a false null hypothesis may occur. Rejection of a true null hypothesis is called a type I error (based on the level of significance α), while the acceptance of a false null hypothesis is called a type II error (denoted as β). This can be shown in the following table (Walpole and Myers 1993).

	H_0 is true	H_0 is false
Accept H_0	Correct decision	Type II (β) error
Reject H_0	Type I (α) error	Correct decision

The acceptable levels of α and β will determine the number of samples needed to do the hypothesis testing. Typical levels of α and β are 0.05 and 0.1 or 0.2, respectively. The power of an experiment is often quoted as a measure of the specificity of the test and it is equal to $1-\beta$.

For this dissertation research, the experiment is to test the ability of various filtration media to remove a variety of pollutants from simulated runoff (for the laboratory investigations) or from pre-settled stormwater runoff. The hypotheses can be stated as follows for each filter column:

H_0:   influent concentration$_i$ = effluent concentration$_i$

H_1:   influent concentration$_i$ ≠ effluent concentration$_i$

where i = pollutant of interest. The result of this hypothesis testing is a two-tailed test for significance (as measured by the value of the test statistic). Although the problem statement implies a one-tailed test (where H_1: influent concentration$_i$ < effluent concentration$_i$), it is important to know if the filter increases the concentration of a pollutant, such as through leaching. The leaching of pollutants from the media itself may increase the concentration of that pollutant in the effluent to a concentration that may cause a problem in a receiving water. For example, the compost that was used in prior projects leaches phosphorus, and the addition of phosphorus, if in significant quantities (concentration and mass loading), may contribute to eutrophication of the receiving water body. This is why the two-tailed test is selected, where the proposal is to test whether or not the effluent is equal to the influent.

The statistical tests used could be those applicable for determining if the means of the two independent populations are equal or not. This is only applicable for a certain portion of the filter run.

Based upon past work and a literature review, the removal efficiency of the filter will remain constant for a specified period of time (usually until a certain portion of sorption sites fill),

and then will begin to decrease. The reason for this decrease is that once a certain fraction of sites fill, the availability of sites for new pollutants to sorb are limited and a contact between the pollutant and the media may result in the pollutant bumping into another, previously-sorbed pollutant, rather than into an empty site. Until this fraction of the total number of sorption sites is filled, the removal efficiency is expected to depend only on the likelihood of a favorable contact between the pollutants in the influent water and the sorption site on the filter medium. The number of samples required for the first part of the breakthrough curve can be estimated using a paired sample calculation, as shown below.

The breakthrough phenomenon is completely different from the ability of a new medium/filter to remove pollutants, although they are related by the sorption capacity of the media and whether the time of contact between the medium and the pollutant is sufficient to allow sorption or ion-exchange to occur. For the laboratory investigations where the simulated runoff is filtered until the sorption capacity is exhausted, the testing of equivalence for the breakthrough curves will be the statistical analysis performed. Since each sample collected throughout the filter run is dependent upon the prior samples, the required number of samples cannot be calculated as though the samples are independent. The goal of the sampling scheme for the laboratory investigations is to collect sufficient numbers of samples that the breakthrough curves can be plotted and an equation can be derived for each medium for each pollutant.

For the pilot-scale work, the filter capacity may not be exhausted for each medium for each pollutant. For this set-up, it is the initial removal efficiency that is to be tested as part of the hypothesis testing. If it could be assumed that the two populations (influent and effluent) are independent during the first part of the filter run, then a systematic random sampling scheme could be used to calculate the number of samples required during the first part of the filter run. The calculation of the number of samples needed for a two-tailed test for systematic random sampling is done using the following equation:

$$n = (Z_{1-\alpha/2} + Z_{1-\beta/2})^2 \sigma^2 / d^2 \qquad\qquad [10]$$

where n = number of samples needed;

$Z_{1-\alpha/2}$ and $Z_{1-\beta/2}$ = x axis coordinates for the two-tailed test that give areas under the normal curve equal to 1-α and 1-β, respectively;

σ^2 = variance of the sample population;

d = acceptable difference from the mean (measured as fraction of the mean).

If it is assumed that each population is independent (since influent and effluent samples are collected from different filter columns, i.e., a blank column is constructed and the influent sample collected after passage through the blank column in order to negate any effects of the column wall material), the determination of the number of samples could be done for each population, influent and effluent. Assuming a degree of confidence of 95% (α = 0.05) and a power of 90% (1-β=0.9), the appropriate Z values are for the two-tailed test, 1.96 and 1.645, respectively.

This equation can be restated, as shown by Gilbert (1987) for the coefficient of variation, as follows:

$$n = (Z_{1-\alpha/2} + Z_{1-\beta/2})^2 \eta^2 / d_r^2 \qquad\qquad [11]$$

where η = coefficient of variation (standard deviation/average);

d_r = relative error ([sample mean - population mean]/population mean);

n and Z have the same meaning as above.

Substituting into this equation, the result is as follows:

$$n = (1.96 + 1.645)^2 \eta^2 / d_r^2 \qquad\qquad\qquad [12]$$

and assuming an acceptable coefficient of variation of 0.5 (refer to Table 1) and an acceptable relative error of 1, the number of samples required of influent or effluent from each filter media (prior to the start of breakthrough) equals 3.245 samples or 4 samples each.

The underlying assumptions of the above equations are that the populations are normally distributed and that both populations (influent and effluent) have the same variance. The assumption of normality is likely not met, since most environmental populations are log-normally distributed and since there is an upper limit on percent removal of pollutants of 100%. However, when the coefficient of variation is small (less than 0.4-0.5) (see Table 23), the results for a log-normally distributed population can be approximated by using the equations for a normally distributed population. The assumption that both the influent and effluent populations have the same variance may not be strictly true, but based on prior sampling as part of the master's work, the variances are very close. The third assumption of the Gilbert equation is that the size of the population is very large relative to the variance. This assumption holds for this sampling scheme.

Table 23. Average Percent Pollutant Removal (Coefficient of Variation in parentheses) – Laboratory-Scale Filters* (Clark 1996)

Parameter	Carbon-Sand	Peat-Sand	Zeolite-Sand	Compost-Sand	Agrofiber-Sand	Sand
Toxicity (filtered)	83 (0.41)	63 (0.5)	100 (0)			
Color (filtered)	26 (0.68)					
Carbonate	47 (0.77)	100 (0)				
Bicarbonate	23 (1.15)	100 (0)				
Chloride		17 (0.29)	7 (0.47)			
Nitrate	97 (0.04)					
Sulfate		5 (0.92)				
Hardness		52 (0.26)				
Potassium	15 (1.11)		39 (0.33)			
Calcium		88 (0.02)	17 (0.57)			
Total Solids		17 (1.28)				
Dissolved Solids		45 (0.29)				
Volatile Solids						23.4 (1.06)
Zinc (unfiltered)	76 (0.24)	71 (0.24)	73 (0.19)	76 (0.14)	77 (0.06)	71 (0.17)
Zinc (filtered)	48 (0.78)	58 (0.57)	62 (0.46)	82 (0.24)	84 (0.23)	88 (0.26)
COD (unfiltered)	96 (0.06)					
COD (filtered)	85 (0.4)					
2,4-Dinitrophenol	43 (1.19)	36 (1.54)				
Di-n-butylphthalate		66 (0.60)				
Bis(2-ethylhexyl) phthalate	90 (0.05)	39 (0.56)	82 (0.16)			94 (0.09)
Pentachlorophenol			79 (0.53)		92 (0.18)	100 (0)
Dieldrin		68 (0.58)				

*Only percent removals greater than zero are shown in this table.

Another way to view the data is to assume that these are paired data, i.e., the influent and effluent to each filter are related. This assumption is also not completely correct because the sampling protocol does not call for collecting the effluent sample after the slug of influent that was sampled has had time to pass through the filter. However, if these were paired data, the appropriate number of samples would be calculated using the following equation:

$$n = 2[(Z_{1-\alpha/2} + Z_{1-\beta/2})/(\mu_1 - \mu_2)]^2\sigma^2 \qquad\qquad [13]$$

where   n = number of samples needed (not number of pairs)

     μ_1 and μ_2 = means of the two sample sets

     σ^2 = variance of the two sample sets (assumed to be equivalent)

     Z has the same meaning as in the above equations

Substituting using the same assumptions as above (coefficient of variation = 0.5, difference in means is μ), the required number of samples is 6.498 or 7 samples. This is equal to needing 3.5 sample pairs (influent and effluent) or 4 sample pairs. The relationship between the required number of sample pairs needed for a power of 80% and a confidence of 95% for different coefficients of variation and the difference in the means is shown in Figure 1. The lines for this figure are calculated in a manner similar to that outlined in Gilbert for random sampling where the variance may not be known, but the allowable error is known, as is the coefficient of variation.
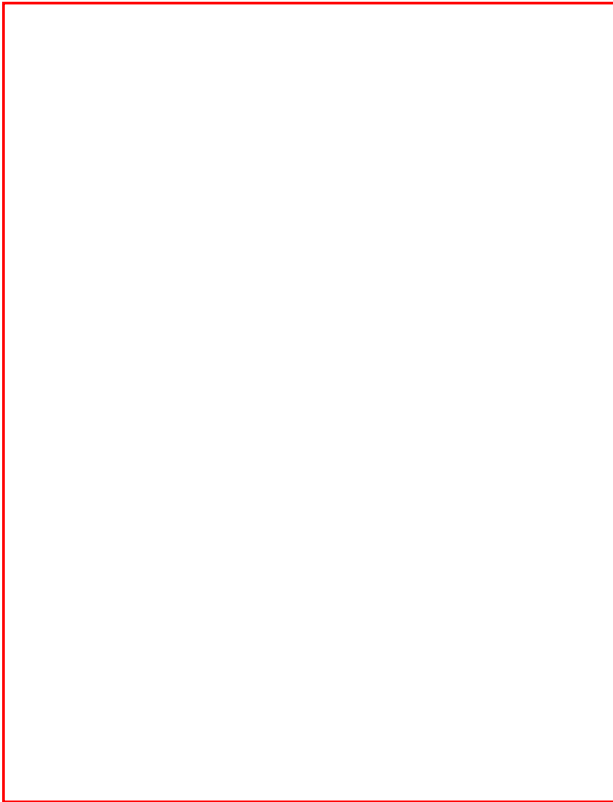

Figure 1. Calculation of Number of Paired Samples

Notice that while neither sampling method is satisfactory for calculating the needed numbers of samples, all the methods indicate that a minimum four samples each of influent and effluent from each medium will be required. For the pilot-scale testing, a minimum of eight sampling events is planned. The exact manner of sample collection is described in the appropriate section below.

Filter Construction and Media Selection for Laboratory Scale Tests

Filter columns containing the various media will be constructed in glass, Kimax-brand, one-liter, graduated burets (ID = 48 mm), giving a cross-sectional area for filtration of 18 cm^2. Filter columns will be constructed first by placing a square piece of fiberglass window screen in the bottom of the buret and filling the buret to the 1000 mL line with epoxy-coated fish tank gravel (3-4 cm depth). A 15 cm deep layer of very fine sand (sandblast grade from Porter Warner Industries, Birmingham, AL) will be added on top of the gravel (fill to 700 mL line) before a 30 cm layer of selected filtration media will be put in the column (fill to 100 mL line). The columns will be constructed using the recommended depths for the Austin sand filter and preparatory times and steps being those of compost filter system, as supplied by CSF Systems, Inc. All sorption media will be mixed with an approximately equal volume of sand in order to maintain a relatively consistent hydraulic conductivity between media. The masses of sorption media used in the prior breakthrough tests are given below, and will be replicated during these experiments.

The media selected for the laboratory studies include the following; activated carbon, peat moss, ammonia-removing zeolite, compost, agrofiber, and sand. The activated carbon and zeolite will be purchased through Aquatic Ecosystems, Inc. (Apopka, Florida); the peat moss through a K-mart or other local garden shop; and the sand from Porter Warner Industries, Inc. (Birmingham, AL). The sand is a very fine sand (sandblast grade). The compost has been supplied by Stormwater Management, Inc. of Portland, OR (formerly CSF Systems, Inc.), while the agrofiber has been supplied by Forest Products Research Lab. The 50/50 v/v mix is used, as it was in the thesis work, to make the hydraulic conductivities in the filters more uniform.

The filter columns will be placed on a specially constructed carousel. The water will be delivered to a flow splitter using a Masterflex® Peristaltic Pump with Masterflex Tygon® tubing. A funnel-type flow splitter has been constructed of Delrin™ plastic. Reinforced Tygon® tubing will be used to deliver the water from the flow splitter to the individual columns. Prior to construction of the carousel and splitter (which was done as part of the master's thesis work), all proposed construction materials (plywood, treated plywood, Delrin™ plastic, reinforced Tygon tubing, fiberglass window screen, black plastic tubing adapters and caps) were leach-tested by soaking representative pieces in 18 MΩ water for approximately 65 hours. Testing of the leachate water showed that the materials were acceptable, with minimal-to-no adverse contamination expected.

Filter Construction and Media Selection for Pilot-Scale Testing

The filtration columns to be used during this scale-up to a pilot scale will be constructed in graduated polyethylene tanks (55 gallon (0.21 m^3)) capacity. These tanks have been purchased from Aquatic Eco-Systems, Inc. in Apopka, Florida. The catalog description of these tanks is as follows:

> Semi-translucent natural polyethylene allows you to see the liquid level from outside these tanks. (The resin used for these tanks is easy to clean and meets FDA standards). They handle temperatures up to 140ºF.... The 55-gallon tank comes with a three-quarter inch spigot valve already fitted. All tanks have 5/32-inch thick walls.

The listed outer diameter for the tank is twenty-one inches (1.75 ft, 0.53 m) and the depth is listed as thirty-six inches (3 ft, 0.91 m). The inner diameter of the tank is calculated to be 20.6875 inches (1.72 ft, 0.53 m) and the surface area of the tank at any cross-section is 2.334 ft^2 or 0.217 m^2.

The filtration columns will be constructed in using the same construction guidelines as was used in the bench-scale tests, i.e., the City of Austin (1988) and CSF Systems, Inc. (1994) requirements. The entry to the valve will be covered with a fiberglass window screen (purchased at a local hardware store) and gravel will be placed in the bottom of the tank to a depth above the top of the spigot (approximately 2 inches or 5 centimeters). Above the gravel will be a six-inch (0.15 m) layer of sand (from Porter-Warner Industries, very fine/sandblast grade). The sand layer will be rinsed to assure that all the very fines are washed out and that the sand layer is well-packed and is not leaking out the spigot. Once the sand layer has been rinsed adequately, a one-foot layer of the medium of choice (usually a mixed media, 50/50 v/v with sand) will be placed above the sand. The filters again will be rinsed thoroughly and will be allowed to "age" overnight. Because of the problems noted during the design of the multi-chamber treatment train (bypassing large amounts of filter area), a layer of a geotextile will be added to the top of the filter. The geotextile shall be cut slightly larger than the top surface of the filter to ensure that the complete surface of the filter is covered. The geotextile selected for this is called a Gunderboom. It was developed by Amoco and used to clean up and contain oil spills. When tested as a filter fabric, it was noted that flow did not begin until the head on the fabric was approximately two inches (five centimeters). After that, the fabric impeded the flow very little as long the holes in the fabric were not clogged. This fabric has been used in the full-scale MCTTs to distribute flow evenly across the filter, which allows the complete filter surface and depth to be used for pollutant removal. A distributor shall be

placed at the end of the influent line to each filter to ensure that flow is distributed across the complete surface area of the filter (inside the Gunderboom). The ratio of column diameter to median filter grain particle size for the sand filter (the media used to determine filter height and column diameter) shall be significantly greater than 100, which, according to other researchers, should be sufficient to avoid significant wall effects (Clark, *et al.* 1992).

The media selected for further study include the following; activated carbon, peat moss, zeolite, compost, agrofiber, and sand. The activated carbon and zeolite will be purchased through Aquatic Ecosystems, Inc. (Apopka, Florida); the peat moss through a K-mart or other local garden shop; and the sand from Porter Warner Industries, Inc. (Birmingham, AL). The sand is a very fine sand (sandblast grade). The compost has been supplied by Stormwater Management, Inc. of Portland, OR (formerly CSF Systems, Inc.), while the agrofiber has been supplied by Forest Products Research Lab. The 50/50 v/v mix is used, as it was in the thesis work, to make the hydraulic conductivities in the filters more uniform.

Additional filter containers to be used include a Jacuzzi filter set (sold by Aquatic Eco-Systems, Inc., Apopka, Florida). The pump on the Jacuzzi filter is advertised as 70 gallons/minute. However, based upon prior experience, the expected performance is about that of the other pump, 10 gallons/minute with a ten to fifteen foot head. Two filter media will be tested in the Jacuzzi filter apparatus, a lightweight (25 lbs/ft^3) sand that is advertised for use with the filter and a mixed media that contains five sizes of media.

Physical Capacity of the Media (Clogging Tests) using Upflow and Downflow Filtration

The purposes of this task are to determine (1) the amount of suspended solids loading on the media that will reduce the flow rate to certain end points; (2) the effect of maintenance, such as disturbing or removing the top 3 – 5 cm of the mixed media, on flow rate, and (3) the effect of operating the columns in an upflow mode, as opposed to the traditional gravity filtration. This task shall be performed for compost [as supplied by Stormwater Management, Inc.], activated carbon, zeolite, cotton textile waste, agrofiber, peat moss, and sand). It shall be performed in the laboratory using laboratory-scale columns. The data generated under this task shall be compared with the results from the pilot-scale field studies and shall be used to calculate the scale-up factors that will enable designers to use bench-scale data to design full-scale filters for actual installation and use.

The columns required for this test shall be constructed as described above. For the upflow filtration, a layer of gravel shall be added to the top of the media. The test water shall be a mixture of red clay and tap water. The red clay has been selected because it is easily visible in the column (and therefore, the depth of filter being used for physical removal can be determined). The test water shall be prepared first by sieving the clay through a 200-μm sieve. The clay that passes through the sieve and is collected in the pan is that which will be used in the tests. The concentration of clay in water shall be approximately 2 g/L, and the test water shall remain well-stirred throughout the test.

Prior to the start of filtering the clay-water mixture, the flow rate of tap water through columns pre-saturated with tap water shall be determined. This shall be done by measuring the amount of time that it takes a specific amount of water to collect at the exit of the column (measure effluent volume and time required to collect that volume) when approximately constant head is maintained on the column. For the upflow set-ups, the flow rate of the tap water shall be maintained at just less than the velocity required to visually fluidize the bed.

Once the initial flow rate has been determined, filtration of the clay-water mixture shall begin. The flow rate through the column shall be determined in the same manner that the initial flow rate was determined (measure effluent volume and the amount of time required to collect the volume). Flow rate measurements and effluent turbidity measurements shall be collected periodically throughout the filter run. The endpoints of interest in this experiment, and where maintenance may be required, is when the flow rate reaches 10 m/day, 5 m/day, and 1 m/day (corresponding to filtering in a five-minute time interval, 3 – 5 cm, 1.5 – 3 cm, and 0.25 – 0.5 cm of stormwater runoff, respectively). When the flow rate through the column reaches 5 m/day, maintenance, such as disturbing the top 3 – 5 cm of media shall be performed. Immediately after any maintenance activity has been performed, a flow rate measurement shall be taken. The media shall be disturbed whenever a medium's flow rate reaches 5 m/day.

At some point, the maintenance of disturbing the media will no longer be effective and the flow rate will continue to decrease. When the flow rate reaches 1 m/day, the visible depth of penetration of the red clay shall be measured and then the top 1 – 2 cm of media shall be removed (the exact amount removed shall be noted in the records for the experiment) and the flow rate measured. Disturbing the media shall occur when the flow rate through the column is less than 5 m/day. The experiment shall be discontinued when the flow rate becomes less than 1 m/day. The depth of penetration of the red clay shall again be measured.

The results of this experiment shall be presented graphically for all the media. The graphs shall show flow rate vs. suspended solids loading (g solids/m^2 filter area) and turbidity versus suspended solids loading. These results shall be used to provide a preliminary estimate of the total suspended solids loading that can occur on the media in the pilot-scale field studies

without the media "clogging" (flow rate reduced to an unacceptable rate).

Residence Time Investigation

The purpose of this activity will be the determination of the optimum residence/contact time for the water and the media. The results of this task will provide a curve of removal efficiency versus contact time (similar to a traditional rate-of-sorption experiment), allowing an efficient contact time to be selected, but which may not be equal to the time required for the media and runoff water to achieve equilibrium and maximize sorption capacity. This task will be performed by suspending known quantities of media in known concentrations of water for different periods of time. One-liter beakers containing pre-settled stormwater runoff water spiked with specified concentrations of pollutants (such as 1 mg/L copper as copper sulfate and 1 mg/L phosphate) shall be made. Known quantities of each medium shall be placed in contact with the spiked tap water for a specified period of time: 1 minute, 5 minutes, 15 minutes, 30 minutes, and 60 minutes. At the end of each designated time, the water and the media shall be poured through a stainless steel mesh strainer (to capture the large particles of the filter medium) and the effluent from that shall be filtered using a 0.45 μm gel membrane filter. The filtrate water shall be analyzed for the following pollutants: copper, iron, nitrate, phosphate, sulfate, hardness, conductivity and pH. The analysis techniques for the samples shall be those listed below.

The results of this experiment shall be presented graphically for all media. The graphs shall show percent removal vs. contact time. These results can then be used to provide an estimate of the desirable contact time for each filter medium. The regression of these curves using Equation (9) will provide the rate constant needed for the BDST modeling of the adsorption/ion-exchange process.

Effect of Influent pH and Ionic Strength

The second activity to be performed is the investigation of the effects of influent pH and ionic strength on pollutant removal efficiency. The experimental design for this activity shall be a full-factorial (2^2) design (high and low pH, high and low ionic strength). The water to be used for the breakthrough testing shall be pre-settled stormwater runoff from Star Lake. Adjustment of the influent pH shall be done with either sulfuric acid (6 N or greater) or sodium hydroxide (6 N or greater). The water shall be spiked with copper (approximate concentration 0.5 mg/L) and phosphate (0.5 mg/L). The influent ionic strength shall be adjusted with seawater salt (evaporated seawater). The sampling runs for this series of tests shall be as follows:

1.   Run 1 – low pH (4.5) and 'normal' ionic strength (no added salt).

2.   Run 2 – low pH (4.5) and 'high' ionic strength (conductivity ~ 5,000 •S/cm).

3.   Run 3 – high pH (9.5) and 'normal' ionic strength (no added salt).

4.   Run 4 – high pH (9.5) and 'high' ionic strength (conductivity ~ 5,000 •S/cm).

For each run, spiked runoff shall be filtered through the media until breakthrough is noted for copper, phosphate, nitrate, and hardness. In addition to the above-listed pollutants, the grab samples shall be analyzed for iron, turbidity, color, conductivity, pH, and suspended solids. The analysis techniques for the samples shall be those listed below.

During these tests, flow rate for each medium shall be noted when the samples are collected (as time to collect a known volume of water). While the runoff is assumed to be low in particulate matter after several days of settling, it is well documented that some particulates, especially those less than 1 μm in diameter, exist. These particulates, along with the potential shrinking or swelling of the media, potentially may affect the flow rate in the media.

The effluent from each of the columns will be collected and tested after approximately a cumulative 4 L, 12 L, 20 L, 28 L, 36 L, and 44 L of water had passed through each column (each 8 L increment is a composite sample). Testing for copper, pH, conductivity, color, and nutrients will be done on a real-time basis, so that potential breakthrough can be monitored and column testing can be discontinued once breakthrough has occurred. Additional tests may be needed based upon the results seen during the low pH breakthrough tests. If they are needed, samples will continue to be collected after every 8 L of water has passed through the column. Samples will be analyzed using the equipment/methods listed below.

Until breakthrough begins, the influent and effluent samples could be considered to be paired samples and the differences between the two sets can be tested using the Wilcoxon signed-

rank test. Once breakthrough begins, the effluent samples are correlated over time, since the more stormwater that is filtered, the smaller the remaining capacity of the filter becomes. These results cannot be compared in a manner similar to that used for samples prior to breakthrough. The breakthrough curve can be modeled using liquid-solid sorption models, the forms of which are similar to a Langmuir or Freundlich isotherm. Once the parameters that describe the breakthrough curve are determined, the parameters for each media can be compared for identical influent conditions to determine if the type of medium significantly influences the sorption breakthrough. Also, the breakthrough curves for a single medium for different influent conditions can be compared. The testing of the parameters shall be done according to the test methods used for determining if two lines are equivalent (see section on 'Statistical Analysis of the Model').

The second statistical test to be performed on this data will be a factorial analysis. The detailed procedure for performing the factorial analysis is given by Berthouex and Brown (1994) and for interpreting the results is given in Box, Hunter and Hunter (1978). Contrast tables shall be constructed and in general, pH, ionic strength, or the interaction of the two shall be considered significant when the calculated effect for each influence was greater than three times the group standard error. Factorial analysis shall be performed for each filter medium for each pollutant of interest using removal efficiency, measured as percent decrease.

Aerobic versus Anaerobic Conditions in the Media

The purpose of this series of tests shall be to determine if the media are able to retain trapped pollutants even if the filter develops an anaerobic environment, either throughout the filter or only in sections of the filter, between storm events. Since these filters cannot be expected to dry completely between storm events, it is likely that in an area with a long interevent time, an anaerobic environment in the pores could occur. Also, if it determined that upflow operation is beneficial (siphon control of the water entering the filter during a storm), it is anticipated that, because the only the top of the filter would be exposed to air (unlike a gravity filter where the top and bottom are potentially exposed to air between storms, an anaerobic environment will develop.

For this set of tests, only a representative subset of the project media will be used: activated carbon, peat moss, compost, and sand. These media were selected because they provided the best overall results during the preliminary work – with sand being used as a comparison to traditional filter material (Clark 1996). The media will be exposed to a concentrated tap water (10 mg/L of lead, copper, zinc, iron, nitrate, phosphate, and ammonia) for several hours. The water then will be filtered through a 0.45-μm gel membrane filter. The difference between the initial sample and the filtrate for each media should be the amount of each pollutant that is sorbed onto the media (a blank sample shall be collected in a similar manner so that the effects of sorption onto the exposure containers can be accounted for in the data analysis). After rinsing with a buffered distilled water, the media shall be exposed to Star Lake water (pre-settled stormwater runoff) for a period of several weeks. One sample of each medium shall be maintained in an aerobic environment where fish tank bubblers will be used to keep the lake water at oxygen saturation. The other sample of each medium shall be exposed to the Star Lake water while in BOD bottles, where it is anticipated that the naturally-occurring living matter in the water will consume the oxygen and create an anaerobic environment.

All of the samples collected for this phase (all filtrates, rinse water, Star Lake water, and initial spiked tap water) shall be analyzed for the following constituents: copper, iron, lead, zinc, nitrate, ammonia, total nitrogen, phosphate, total phosphorus, pH and conductivity. Sample analysis shall be performed as described below. In addition to the samples listed above, the bottles with the media that were exposed to aerobic and anaerobic conditions shall be measured for dissolved oxygen concentration and oxidation-reduction potential at the end of the several weeks' exposure. The DO and ORP results will be used to determine if an anaerobic environment had developed in the BOD bottles. If an anaerobic environment has not developed, the experiment will continue for at least one more week.

The results for each medium can then be compared statistically (as independent samples) to see if the development of anaerobic conditions in/on the filter medium causes significant pollutant leaching.

Testing of the Pilot-Scale Device

The filters shall be constructed as described above. During sampling, in order to regulate the flow to each filter and to ensure that the influent is not significantly different between filters, test water shall be pumped through a manifold where it will be randomly split into the feed lines for the different filters. This manifold will have in-line flow meters installed, and gate valves will be used to control the flow to each filter.

Testing on the pilot-scale filters shall be performed on a basis that can be expected to simulate the intermittent use that they will receive in a full-scale application. A minimum of eight filtering events shall be performed. The filters shall be transported to the field sampling location and the sump pump installed in the detention pond. Once the set-up is completed, this settled stormwater runoff shall be filtered for approximately eight hours. Grab samples of approximately 1 L shall be collected every hour from the effluent of each filter and shall be combined in a cleaned, 8-L Nalgene jug (one per media) to form a composite sample of the effluent from that day's sampling. A similar composite sample shall be collected of the influent water to the filters. Sample collection shall be in accordance with *Standard Methods for the Examination of Water and Wastewater*. At the end of the day's sampling, the composite samples shall be transported back to the laboratory for analysis.

It is anticipated that this task will last for four to five weeks, with a total of eight sets of samples collected per filter. The filters shall be tested until one of the following endpoints occurs: (1) physical clogging; (2) chemical breakthrough for several pollutants; or (3) end of the project. By testing these filters intermittently for several weeks, it can be shown, by comparing to the laboratory breakthrough testing where water was filtered continuously, if drying between filtration/storm events enhances, degrades, or does not affect pollutant removal efficiencies.

The proposed sampling locations will be area detention ponds, Star Lake and Georgetown Lake in Hoover. These will be chosen based upon accessibility (permission to set up the trailer with the filters has already been granted by the City of Hoover, Alabama) and the likelihood of measurable concentrations of the pollutants of interest. Influent will be delivered to the filters using two sump-type pumps (proposed pump has a measured delivery of 10 gallons/minute with a ten to fifteen foot head), except for the Jacuzzi filters which have separate pumps. Tensiometers will be installed in each filter to measure the percent saturation of the media on a real time basis. Samples will be collected in 8 L Nalgene jugs. Once the samples are collected, they will be transported to the laboratory where they will be split and preserved as required for the analyses.

In addition to the composite samples, grab samples will be collected every other hour during a sampling event. These grab samples shall be analyzed in the field for turbidity, conductivity, and pH. Also, every other hour, the flow rate through the filter (estimated with the effluent flow rate) and the depth of water on top of the filter shall be measured.

The proposed analyses include the following (* indicates that the analysis will be done on both the filtered and unfiltered fractions):

Physical (turbidity*, pH, color*, conductivity, toxicity*)

Anions and Cations (nitrate, phosphate, sulfate, ammonia, magnesium, calcium)

Solids (total, dissolved, suspended, volatile total, volatile dissolved, volatile suspended, particle size distribution)
Metals (zinc*, copper*, lead*)

Organics (chemical oxygen demand*)

E. coli and *Enterococci*

Once the samples reach the lab, they will be homogenized through mixing and then split among seven bottles per sample (three amber glass, four HPDE plastic). Two of the amber glass and one of the plastic bottles will be stored as is at 4°C until analysis. One of the plastic bottles will be preserved with 6 M HNO_3 until the sample pH < 2 (approximately 1 mL). The remaining three bottles will be composited and filtered through a 0.45 μm gel membrane filter. After filtration, they will be split among the three bottles. One amber glass and one plastic bottle will be stored at 4°C while waiting for further analysis. The other bottle will be preserved with 6 M HNO_3 until the sample pH < 2 (approximately 1 mL).

The protocols to be followed for analysis and holding times are listed in at least one of following documents:

EPA Methods and Guidance for the Analysis of Water (EPA 821/C-97-001; 1997)

Handbook of Sampling and Sample Preservation of Water and Wastewater (EPA 600/4-82-029, 1982, and including later additions)

Methods for Chemical Analysis of Water and Wastes (EPA 600/4-79-020; revised 1983, and including later additions)

Quality Assurance Project Plan: Effects, Sources, and Treatability of Urban StormwaterToxicants (Parmer and Pitt 1995)

Quality Assurance Project Plan: Natural Media Filtration (Clark 1999)

Standard Methods for the Examination of Water and Wastewater, 19th Edition (APHA, AWWA, WEF, 1997)

Sample Analysis

Samples collected in the different phases of this research shall be analyzed according to the following analytical protocols (Table 24). Additional information regarding these procedures can be found in the UAB laboratory SOPs (*Laboratory Safety and Standard Operating Procedures: UAB Water Quality Research Laboratories*. R. Pitt and S. Clark. University of Alabama at Birmingham, Department of Civil and Environmental Engineering, Birmingham, AL, 1998). These procedures have been reviewed and accepted by the US EPA (Quality Assurance Project Plan (QAPP) for the phases of this project that they are funding), as well as by the Water Environment Federation (co-sponsor of this research project).

Table 24.   Analytical Techniques

Analytical Parameter	*Analysis Method* **(EPA Method number shown if available; equivalent Standard Methods method in parentheses, if available)**
pH	EPA Method 150 (*Standard Methods* 4500-H$^+$.B.)
Conductivity	EPA Method 120.6 (*Standard Methods* 2510.B.)
Turbidity	EPA Method 180.1 (*Standard Methods* 2130.B.)
Color	EPA Method 110.3 (*Standard Methods* 2120.C.)
Phosphate	EPA Method 365.2 (*Standard Methods* 4500-P.E.)
Nitrate	EPA Method 353.3 (*Standard Methods* 4500-NO$_3^-$.E.)
Ammonia	EPA Method 350.2
Hardness	EPA Method 130.2 (*Standard Methods* 2340.C.)
Toxicity	Microtox™ Rapid Toxicity Screening Procedure as described in the UAB Laboratory SOP
Copper	*Standard Methods* Method 3500-Cu.E.
Lead, Cadmium, Zinc, Copper, Chromium, Iron, Calcium and Magnesium	ICP (*Standard Methods* 3500)
E. coli and *Enterococci*	IDEXX Methods as described in the UAB *Laboratory SOP*
Chemical Oxygen Demand	EPA Method 410.4 (*Standard Methods* 5220.D.)
Solids (Total, Dissolved, Suspended, Volatile)	EPA Method 160.1 and 160.2 (*Standard Methods* 2540.B.C.D.E.)
Particle Size Distribution	*Standard Methods* 2560.B. (using Coulter Counter as described in the UAB *Laboratory SOP*)

Statistical Analysis of the Model

The two design equations (Equations 1 and 8) to be used in the model either are in linear format or can be linearized as follows:

Equation 1: $q = k_i \bullet L_m^{-c}$ [1]

Equation 8: [8]

For Equation 1:

$\ln(q) = \ln(k_i \bullet L_m^{-c})$ [13]

$\ln(q) = \ln(k_i) + \ln(L_m^{-c})$ [14]

$\ln(q) = \ln(k_i) - c \bullet \ln(L_m)$ [15]

For Equation 8:

[8]

The statistical analysis to compare between the media (to see if the choice of the filtration medium affects the time until the media is 'clogged' or the time to breakthrough for chemical capacity) is two-fold. First, the slopes of the regression lines of the media (regression equation form: $Y = \beta_0 + \beta_1 X$, where X equals the natural log of L_m in equation 1 and the natural log of $[(C_0/C_b) - 1]$ in equation 8) can be compared to each other to see if they are statistically significantly different (Kleinbaum, et al. 1998). The hypothesis testing for this using equation 12 would be the following (the subscripts 1 and 2 denote the two different media being compared):

H_0: $c_1 = c_2$

H_1: $c_1 \neq c_2$

Using equation 8 to compare between media, the hypothesis for testing would be as follows:

H_0: $(1/kC_0)_1 = (1/kC_0)_2$

H_1: $(1/kC_0)_1 \neq (1/kC_0)_2$

The test statistic is then given by the following:

[16]

where n = number of observations used to construct the breakthrough curve

β_{1i} = slope of the regression line for media i

$S^2_{Y/Xi}$ = residual mean-square error for media i

S^2_{Xi} = variance of X's for media I

The test statistic, T, should be distributed as a Student's t with (n1 + n2 – 4) degrees of freedom when H0 is true. The statistical test is then:

$|T| > t_{n1 + n2-4, 1-(\alpha/2)}$ where $\alpha = 5\%$.

Second, the intercepts of the regression lines of the media (regression equation form: $Y = \beta_0 + \beta_1 X$, where X equals the natural log of L_m in equation 1 and the natural log of $[(C_0/C_b) - 1]$ in equation 8) can be compared to each other to see if they are statistically significantly different. The hypothesis testing for this using equation 12 would be the following (the subscripts 1 and 2 denote the two different media being compared):

H_0: $\qquad \ln k_{i1} = \ln k_{i2}$

H_1: $\qquad \ln k_{i1} \neq \ln k_{i2}$

Using equation 8 to compare between media, the hypothesis for testing would be as follows:

H_0: $\qquad (N_0 D/1000\varepsilon v C_0)_1 = (N_0 D/1000\varepsilon v C_0)_2$

H_1: $\qquad (N_0 D/1000\varepsilon v C_0)_1 \neq (N_0 D/1000\varepsilon v C_0)_2$

The test statistic is then given by the following:

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ [14]

where $\quad n$ = number of observations used to construct the breakthrough curve

$\qquad \beta_{0i}$ = slope of the regression line for media I

$\qquad \boxed{}$ = mean of the X values for each equation

$\qquad S^2_{Y/Xi}$ = residual mean-square error for media i

$\qquad S^2_{Xi}$ = variance of X's for media I

The test statistic, T, should be distributed as a Student's t with $(n_1 + n_2 - 4)$ degrees of freedom when H_0 is true. The statistical test is then:

$\qquad |T| > t_{n1 + n2-4, 1-(\alpha/2)}$ $\quad$ where $\alpha = 5\%$.

The use of the t-distribution generally assumes that the samples are normally distributed. If it is assumed that the samples are log-normally distributed but with a low COV, the normal approximation will hold. If the normal and log-normal distributions are not found to be applicable to these results, then nonparametric methods will have to be used to compare the slopes and the intercepts of the design equations for each medium.

The tests described above will allow for comparison of the various regression lines generated during the laboratory work. Should groups of equations (such as between media) not be statistically significant from each other, then the media can be categorized according to parameter groupings. For the design engineer, these groupings have the potential to be very useful for estimating the design equations for a media combination that was not tested but that can be assumed to behave like a specific category of media (for example, possible groupings may be organic media, granular inorganic media, fibrous media).

Statistical Analysis of the Pilot-Scale Results

Once the samples are collected, the results must be analyzed. Since the populations may not be normally distributed, the traditional Student's t-test cannot be done unless the normal distribution is confirmed. If the results are found to be log-normally distributed, then a t-test could be used on the log-transformed data. The normality assumption for both the

untransformed and log-transformed data would have to be done using a goodness of fit test for normality, such as the Kolmogorov-Smirnoff test.

The problem is that there are so few data points to analyze. A sample size of eight or less (the potential exists for both the influent and effluent to be less than the limit of detection for one or more analytes thus rendering the pair unusable) restricts the ability of any statistical test to predict normality within an acceptable range of P values (such as the traditional 0.05). The preferred analysis, and the one that will be used on this data, is a nonparametric test such as the Wilcoxon signed-rank test. The nonparametric tests make no assumptions regarding the underlying distribution.

The Wilcoxon signed-rank test, as described by Gilbert (1987) may be used to test for differences in two independent populations, i.e., if the measurements from one population are consistently larger or smaller than the measurements from the other. In this instance, the question is if the influents are consistently larger or smaller than the effluents. It is an alternative to the Student's t-test when the underlying distribution is not known. Another advantage of the Wilcoxon signed-rank test is that it can handle a limited number of 'non-detects' in the laboratory results. This is crucial when working with stormwater runoff, especially pre-settled runoff, as many of the pollutants are present in the water in concentrations approaching the method detection limit. The likelihood of receiving 'non-detects' is great and the method of data analysis must be able to deal with this phenomena. The procedure for performing the Wilcoxon signed-rank test are given in Gilbert (1987) on page 248 or in Lehmann and D'Abrera's book *Nonparametrics: Statistical Methods Based on Ranks* (Holden-Day, 1975). The Wilcoxon signed-rank test was also the test used to analyze the data from the master's thesis work. Use of this test to analyze the dissertation data makes the results immediately comparable between the two, and this comparison can be used to answer specific questions that have arisen from the master's work, such as the effect of the narrow columns (i.e., wall effects, filter bypassing) on sample flow, contact time and time required for sorption. Large changes in which removal are statistically significant will indicate that the small columns used in the bench-scale studies were too small to adequately replicate the filter media ability in field conditions.

The field data can also be compared to the model/design equations that have been developed during the laboratory work. Predicted versus experimental values can be compared statistically to see if the model is adequate at predicting the removal efficiency of pilot-scale filters. The results of these comparisons may provide an indication of any effects that scale-up from a laboratory (or bench-scale) apparatus to a pilot-scale set-up may have had on the model predictions.

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